

From Threat to an Asset: Water in Steelworks

How modern steelworks can improve water related performance via benchmarking and development of High Density Sludge (HDS) Process

by

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Summary

The Water Framework Directive (WFD) 2000/60/EC is set to overhaul the management of the water environment within the EU. Following its enforcement in 2015, changes are expected to the current water related regulations and water intensive industries, including steelworks, ought to prepare themselves for changes.

In 2007 Corus Group was taken over by Tata Steel, now one of the World's top 10 steel producers with its production of 31 MTPA (million tonnes per annum of crude steel). Tata Steel Port Talbot Integrated Steelworks is one of Tata Steel's main sites, currently producing some 4.33 MTPA (in 2007) of crude steel (slab) and is a major user of water with its 8 production facilities and supporting functions.

From 2007 to 2011 the author worked as a core member of the World Steel Association Water Management Project. The project included development of a survey to gather water-related data from the World's steelworks. 29 steelworks took part in the survey and using the data, an extensive assessment of water related performance in steelworks around the World has been carried out. The findings show that water performance related figures, including water use and effluent generation, vary from under 1 to near 150 m³/ts. The average consumption figure being 28.4 m³/ts with once-through cooling using an average 82% of this water. The average effluent discharge figure is 25.4 m³/ts. For Port Talbot Steelworks these figures are 33.8 m³/ts and 28.8 m³/ts respectively.

An investigation into effluent treatment technologies and efficiencies included carrying out chemical precipitation and co-precipitation titration experiments, especially looking at zinc, in order to better understand the behaviour of relevant metals during hydroxide precipitation reactions. The experimental results were compared against PHREEQCi theoretical geomodelling precipitation prediction data and PHREEQCi 2 indicated minimum zinc solubility is reached at pH 9.5. Laboratory experiments support this. Iron enhances zinc precipitation strongly via co-precipitation. A similar effect, although to a lesser extent, is achieved for zinc co-precipitation with nickel and lead.

The author's study of the Port Talbot water systems established that the chemical precipitation processes in operation leads to the generation of voluminous sludge that is hard to dewater further. This prompted the initiation of an investigation into the suitability of the High Density Sludge (HDS) process in treating high volume, non-acidic low metal concentration effluents, such as steelworks final effluent. Prior to this research the HDS process has been used mainly for the treatment of mine effluents and its suitability in treating non-acidic, low metal concentration effluent has not been fully explored. During the trial, a 10 L/h influent feed rate was aimed for with a half hour retention time at the first two reactors. The flocculant feed rate was around 2.5-3 mg/l of treated effluent throughout the trial. At the end of the trial the sludge concentrations exceeded 17% (w/w), while the treatment efficiencies of zinc and other metals stabilised and improved. Furthermore, the sludge was behaving as HDS sludge achieving high settling rates in excess of 22 m/h at 5% (w/v). Solids concentrations and sludge filterability had improved with the specific cake resistance reducing from the 'single pass' precipitation sludge near 35,000 Gm/kg to the 777 Gm/kg after 2 weeks of trial to a mere 169 Gm/kg at the end of the HDS trial.

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1 INTRODUCTION

In 2007 Corus Group was taken over by Tata Steel which lifted Tata Steel into the top 10 steel producers in the World and is currently (2010) the World's 7th biggest steel producer, with its production of 31 MTPA (million tonnes per annum of crude steel). Tata owns two integrated steelworks in Europe, one being Tata Port Talbot Steelworks and the other being Tata Ijmuiden Steelworks. Within the Port Talbot Steelworks, the steel is made via the BOS production route via seven different facilities into high grade strip steel as will be explained in Chapter 2 which provides background to this study.

Due to freshwater scarcity, new paradigms in water resources management are implemented within steelworks around the World. Furthermore, with water high on the agenda for governments and local authorities alike, additional pressure to reduce water abstraction and tighten discharge consent limits are being enforced via legislation. In order to get an understanding of the current and future legislative demands, Chapter 2 outlines legislation that sets guidelines and consents for water and effluent discharge amongst other things. The chapter also gives an update on developments to the Water Framework Directive (WFD), the newest water legislation to regulate industry. Chapter 2 also provides a short background to effluent treatment options generally available for industrial water treatment.

Tata Port Talbot Steelworks is a complex integrated steelworks with a large area and several water intensive processes and wastewater discharge flows and points. Chapter 3 provides a critical assessment of the Port Talbot Steelworks water and effluent systems, whilst also providing results on the performance of the effluent systems and the final effluent treatment system.

Water is an important utility for the iron and steel making process, where water is used for several things including equipment cooling and material processing. Water consumption within steelworks ranges from approximately 1 m³/tonne of steel (ts) to above 150 m³/ts and these figures vary from location to location depending on several factors. In some cases, with very little fresh water availability, the cooling water used in

steelworks is running in a closed circuit cooling system. This leads to reduced water consumption, sometimes reaching less than 5 m³/t steel as will be explained in Chapter 4, which also gives information on Worldsteel Association's (former International Iron and Steel Institute) Water Management Project, its members and survey development for gathering data and results on benchmarking of the World's steelworks.

Disposal of wastewater is the least favorable option for its management purposes, but no matter how much wastewater is reused and recycled, there will always be some wastewater that will need to be treated. Within steelworks several difficult effluents arise during production that require their own treatment and the final effluent should be treated to a sufficient quality prior to discharge to the environment. Effluent treatment is not generally seen as an important factor for the development of water management activities within steelworks around the World as explained in Chapter 4. Within Tata Port Talbot Steelworks however, the final effluent treatment and the sludge generated during the treatment has a great importance due to tightening legislation on effluent discharge consent limits and sludge landfilling requirements which is outlined in Chapter 3.

'Conventional chemical precipitation' remains the most common industrial effluent treatment method to date. In order to understand the behaviour of this type of treatment, Chapter 5 gives details on hydroxide precipitation to establish how metals behave during precipitation and co-precipitation and give information on what the right pH is for removal of relevant metals during individual and co-precipitation. Results on precipitation and co-precipitation experiments and their comparison against theoretical results from PHREEQC will also be presented in Chapter 5.

The conventional chemical precipitation achieves good treatment efficiencies with little capital expenditure and moderate operational expenditure, depending on the alkali in use, but the sludge generated during operation is voluminous with typically maximum settled sludge solid concentration of between 1% and 5% solids and the sludge is difficult to dewater further. The disposal of this sludge generated during conventional precipitation can be costly and long-term storage can cause issues due to metals being leached out and released under certain conditions. This has lead to the development of

the High Density Sludge (HDS) process, which although essentially a chemical precipitation process, produces sludge with different physical and chemical characteristics. These include improved solid crystallization and increased solids concentrations of between 15% and 35%. Due to the changed sludge properties, the sludge settlement characteristics and dewaterability is greatly improved.

The use of High Density Sludge (HDS) process on steelworks final effluent will be outlined in Chapter 6, which will give information on the process, including the important process parameters, its applications and benefits. The chapter will outline results on a staged HDS process pilot experiment that used feed mimicking steelworks effluent and showcase the findings on the use of HDS process for final effluent treatment at steelworks. Furthermore, the chapter will discuss how conventional precipitation and HDS process sludge dewatering capabilities were tested using filtration. The chapter will finish by giving results on filter-pressing experiments.

Finally, Chapter 7 concludes the previous chapters of the dissertation.

2 BACKGROUND

2.1 UK Water Related Legislation

Water related issues have been under a great deal of focus in the European Union during recent years and a number of new pieces of legislation relating to water have been integrated into national legislative framework. This has and will be putting industrial facilities under pressure to meet continually tightening regulations and become more sustainable with water-related matters.

United Kingdom environmental policy has undergone a revolution since the introduction of the 1990 Environment Protection Act and is still evolving, driven by the legislation from the European Union in the form of EU directives. The formation of the Environment Agency brought together for the first time, the different regulatory authorities responsible for atmospheric, solid and wastewater discharges.

At present, there is a wide range of European legislation covering several different aspects of water management. This is widely acknowledged as a patchy and inconsistent approach. Cashman (2006) states that, several water companies and even the Government has acknowledged, through the establishment of the Better Regulation Task Force, that there might be room for improvement in the present water regulations.

The management of the water environment within the EU is set to be overhauled by the Water Framework Directive (WFD) 2000/60/EC, which is due to be fully enforced within the UK by 2015. Following the implementation of the WFD, changes are expected to the current water related regulations and water intensive steel industries should prepare themselves for changes early on.

2.1.1 Environment Agency

The Environment Agency (EA) was established in 1996 by merging the National Rivers Authority (NRA) and Her Majesty's Inspectorate of Pollution (HMIP) and The Waste Regulation Authority (Gray, 2000). In England and Wales the Environment Agency is

responsible for maintaining or improving the quality of so called ‘controlled waters’, which are defined in section 78A(9) of the Environment Protection Act 1990 (HM Government, 1990) by referencing Part III (Section 104) of the Water Resources Act 1991 (HM Government, 1991) to include fresh inland, territorial marine, underground water and coastal waters. The Environment Agency enforces its responsibilities to industry through environmental regulations.

The following topics will introduce the main parts and pieces of legislation that have an impact on the water related activities of integrated steelworks within the UK.

2.1.2 Environmental Protection Act 1990

The Environmental Protection Act (EPA) 1990 was introduced in order to control the amount of dangerous substances entering the environment. Part I of the EPA 1990 introduced a regime known as Integrated Pollution Control (IPC) and it covers releases to air, water and land.

IPC controls the most polluting industrial processes, which are set out in the Environmental Protection (Prescribed Processes and Substances) Regulations 1991, which also lists the dangerous substances in its Schedule 5. The Water Resources Act 1991, controls discharges direct to controlled waters, except for those that are covered under IPC. Controlled under Part I of the EPA 1990 in addition to the regulation of prescribed processes, are the substances within the ‘red list’ (introduced in 1989) (Crathorne et al., 2001), which is outlined in Environmental Protection (Prescribed Processes and Substances) Regulations 1991. According to Argent et al. (2004), the substances on the red list are considered to be so toxic, persistent or liable to bio-accumulation within the environment that steps should be taken to fully eliminate their discharge to water.

2.1.3 Dangerous Substances Directive 1976

The Dangerous Substances Directive (76/464/EEC) was adopted in 1976 to provide a framework for eliminating or reducing pollution of inland waters. Chemicals are placed

into two lists in this Directive; DS List I or ‘Black List’ or DS List II or ‘Grey List’ (Crathorne et al., 2001). List I is considered to be the more important one of the two and has limit values and environmental quality standards agreed at Community level. List II chemicals are controlled using environmental quality objectives and quality standards agreed nationally.

2.1.4 Integrated Pollution Prevention and Control

The European Union’s Integrated Environmental Directive through the Integrated Pollution Prevention and Control (IPPC) Directive 96/61 regime updated the system of Integrated Pollution Control in 1996. The aim of the IPPC Directive is the prevention or minimising of environmental pollution caused by industrial installations by means of source-targeted measures and therefore, the monitoring of process effluents and wastewater discharges is required under the Integrated Pollution Prevention and Control (IPPC) Regulations. According to Kat (2005), the purpose of the IPPC was to create a European Union level playing field for industrial permitting.

The IPPC Directive operates under The Pollution Prevention and Control Regulations and it is made effective by granting permits to industrial installations. In order to gain a permit, the company has to demonstrate in its application, in a systematic way, that the techniques it is using, both represent the use of Best Available Techniques (BAT) taking account of relevant local factors, and meets other relevant statutory requirements (Environment Agency, 2004). The Directive also introduces other new terms, including Best Reference Document (BREF) and Level Playing Field (imposing equal demands on like installation within the EU) (Kat, 2005).

Tata Port Talbot Works IPPC Permit includes consent limits for wastewater flow as well as for several wastewater constituents for different discharge points as will be outlined in Chapter 3.

As this study is concentrating on metals, Table 2.1 lists relevant metals that are included in the DS List I, IPPC and other legally driven priority lists, including the WFD Directive, which will explained in depth later in this Chapter.

Table 2.1 Relevant metals included in the UK law (Adopted from Crathorne et al., 2001)

Substance	DS List I	DS List II	UK prescribed substances	IPPC	WFD
Cadmium	X		X		X
Copper		X			X
Lead		X			X
Nickel		X			X
Mercury	X		X		
Mercury compounds				X	
Zinc		X			
Iron		X			

2.1.5 Water Act 2003

Governmental concerns regarding the responsible use of water are reflected in the Water Act 2003, which changed the UK water abstraction system. Now the abstractions are regulated through licences, which were enforced by the Water Act 2003. Anybody who abstracts more than 20 m³ of water per day from ground or surface waters in Wales or England must have an abstraction licence from the Environment Agency as stated in the Water Act 2003 Part 1. There are costs involved in abstraction and the annual subsistence charge is payable by everyone who holds a license to abstract or impound water.

The Environment Agency (2011a) states that the subsistence charge is calculated by multiplying the following factors together:

- Volume – annual licensed volume (in ‘000 cubic metres),
- Source – unsupported, supported or tidal,
- Season – summer, winter or all year,
- Loss – high, medium, low or very low and
- Standard unit charge (SUC) – location-specific multiplier for the abstraction point.

The abstraction charges for 2011/2012 throughout England and Wales are as listed in Table 2.2.

Table 2.2 Abstraction charges for 2011/2012 in Wales and England (Environment Agency, 2011a)

Region	SUC (£/1000 m³)
Anglian	24.51
Midlands	14.95
Northumbria	25.98
North West	12.57
South West (including Wessex)	19.71
Southern	19.23
Thames	13.84
Yorkshire	11.63
EA Wales	13.89 ¹

2.1.6 Water Framework Directive

The Water Framework Directive establishes a framework for the Community action in the field of water policy (European Union, 2010). WFD is the most substantial piece of EC water legislation to date. It requires all inland and coastal waters to reach "good status" by 2015. It will do this by establishing a river basin district structure within which demanding environmental objectives will be set, including ecological targets for surface waters (Defra and WAG, 2006). Any organisation with an abstraction licence or discharge to the water environment will be affected.

The Water Framework Directive aims at:

- Expanding the scope of water protection to all waters, surface waters and groundwater,
- Achieving "good status" for all waters by a set deadline,
- Water management based on river basins,
- Using a combined approach of emission limit values and quality standards and
- Streamlining legislation.

By rationalising and updating the current water legislation, a number of existing European directives will be replaced by the WFD. Examples of these can be seen below.

¹ Up from 12.85 in 2007/2008

Replaced by the end of 2007 (European Union, 2008):

- Surface Water Abstraction Directive – 78/659/EEC
- Surface Water Abstraction Measurement / Analysis Directive – 79/869/EEC
- Replaced by the end of 2013:
- Groundwater Directive – 80/68/EEC
- Discharge of Dangerous Substances Directive – 76/464/EEC

As seen above, the WFD incorporates the Discharge of Dangerous Substances Directive 76/464/EEC, which requires member states to reduce or eliminate discharges of several metals to the environment.

Successful implementation of the Water Framework Directive will go a long way in protecting all elements of the water cycle and enhancing the quality of groundwaters, rivers, lakes, estuaries and seas and it should be noted that due to this Directive, the Environment Agency will be enforcing an ever tightening approach to water and wastewater related issues that will have an appreciable effect especially in industrial facilities.

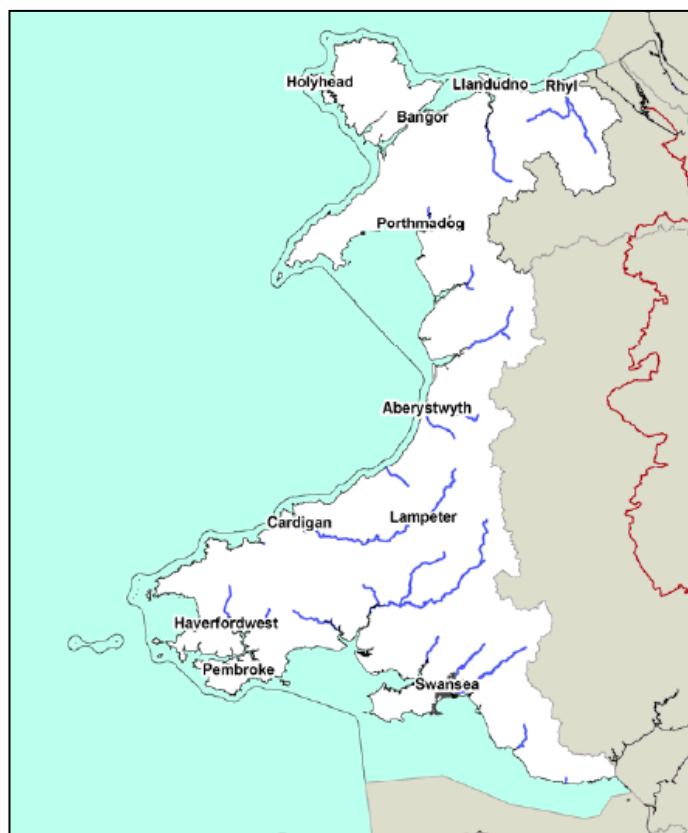


Figure 2.1 West Wales River Basin District (Environment Agency, 2009)

2.1.6.1 River Basin Management Plans

The Water Framework Directive will introduce the concept of integrated river basin management based on each of the 11 River Basin Districts in England and Wales. The Port Talbot area belongs to the West Wales district, which can be seen in Figure 2.1. Each River Basin District will be treated as its own entity and, as mentioned before, the aim is that every District will achieve ‘good ecological status’ by 2015.

2.1.6.1.1 Classification of River Basin Management Districts

The WFD requires looking at the water environment as a whole, integrating water quality, quantity and physical habitat with ecological indicators. The WFD assesses the status of waters by looking at ecological, chemical and physical elements using new and updated classification systems. As can be seen in Figure 2.2 surface water bodies will be assigned to one of five ecological status classes of ‘high’, ‘good’, ‘moderate’, ‘poor’ or ‘bad’. The status will be determined by the element, which received the worst classes’. Further to the ecological status, two chemical status classes of ‘good’ and ‘not good’ will further classify the status of the water body. In order to achieve the overall aim of ‘good status’, surface water will have to be at least ‘good’ for ecological and chemical status (Defra and WAG, 2006).

According to Environment Agency (2006), the Directive requires to ‘aim to achieve’ good status for surface and ground waters (or, in some cases, good ecological potential) by 2015. However, it should be noted that the Directive recognises that there may be conditions under which achievement of good status by 2015 may not be possible. It therefore includes a system for agreeing extensions to the deadline for achieving good status and/or setting lower environmental objectives over a continuous series of management cycles. After the first cycle to be completed by 2015, each subsequent cycle will take six years, from 2016 to 2021, 2022 to 2027 and so on. Long-term approach is endorsed by the Environment Agency, but as many improvements as possible are wished to happen within the earlier cycles.

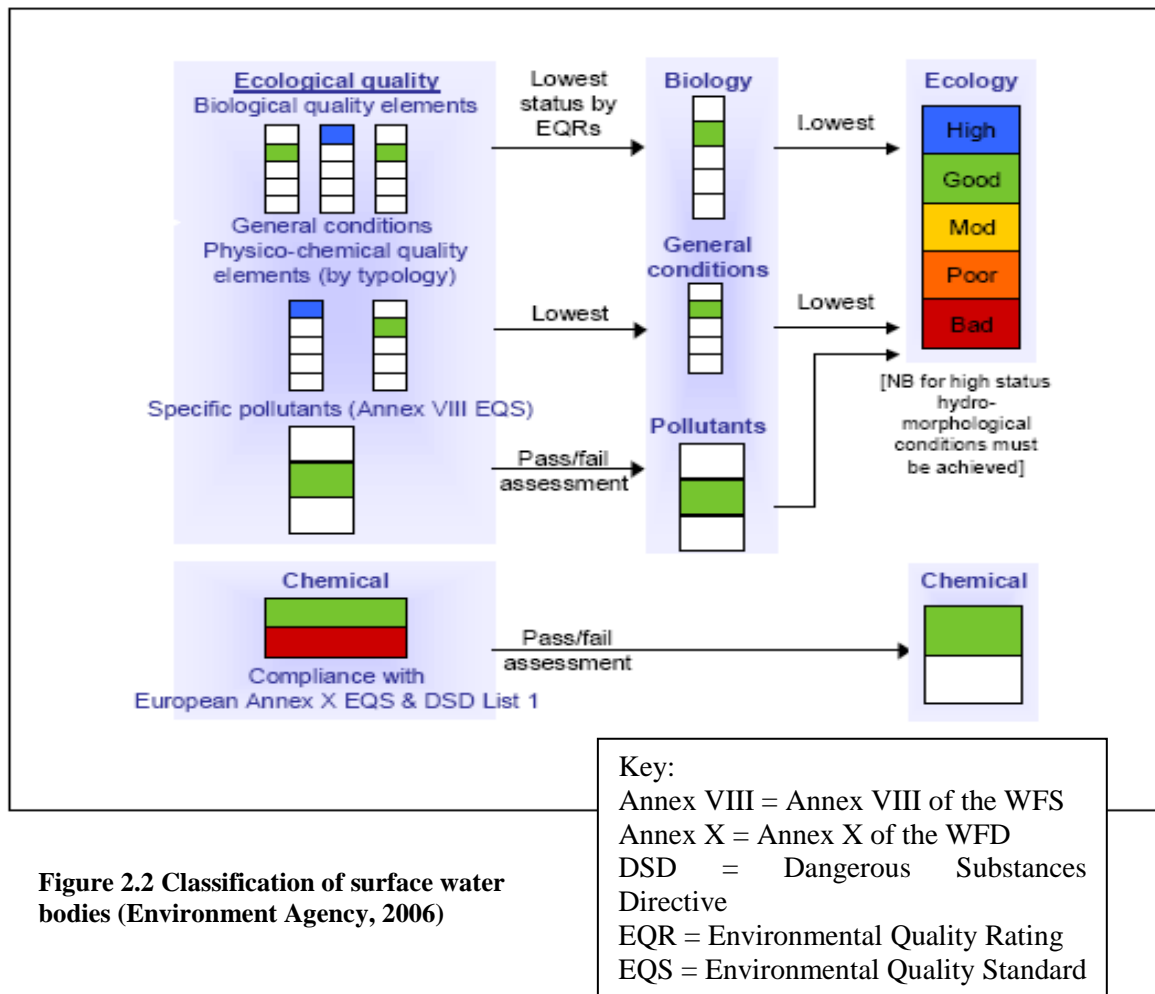


Figure 2.2 Classification of surface water bodies (Environment Agency, 2006)

2.1.6.1.2 Timescale for the River Basin Management Plans

It is impossible to create a better water environment overnight. The Water Framework Directive timetable is a long-term programme of environmental improvement. The timeline of the first River Basin Management Plans (RBMP) can be seen in Figure 2.3.

The most important dates for the implementation of the WFD include (Defra and WAG, 2006):

- 2008 (22nd Dec-June 2009) Consult on draft RBMP, which includes overview of status and programmes of measures.
- 2009 (Dec) first RBMP, including the setting of environmental objectives for each body of water and summaries of programmes and measures.
- 2012 the management plans for all of the river basins to be operational.
- 2015 meet Directive objectives for the first RBMP.

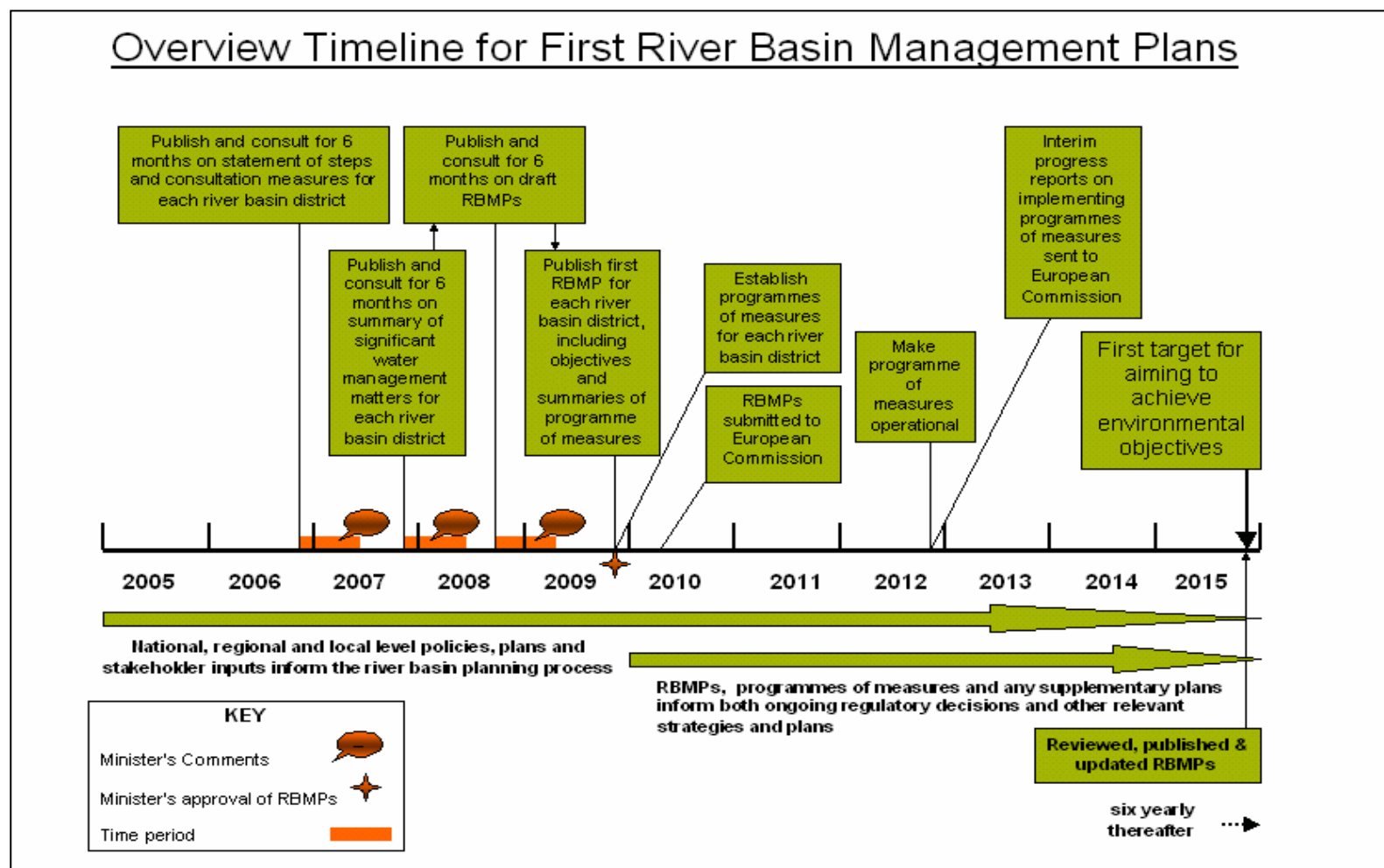


Figure 2.3 Overview of the first RBMPs timeline (Defra and WAG, 2006)

2.1.6.1.3 Priority Substances

The Water Framework Directive is expanded further by two ‘daughter’ directives, one aimed at protecting groundwater (Directive 2006/118/EC), the second at reducing pollution of surface water (rivers, lakes, estuaries and coastal waters) by pollutants on a list of priority substances.

The biggest impact that the Water Framework Directive is expected to have on industrial facilities is tightening of consent limits on discharges. The Annex X of the Water Framework Directive (WFD) 2000/60/EC outlines the original list of 33 priority substances (or groups of substances) identified. 11 of these were so-called priority hazardous substances, 14 are priority hazardous substances that are under review and 8 are priority substances (European Parliament and Council, 2000). Decision 2455/2001/EC amended the list of priority substances and the Directive on Priority Substances 2008/105/EC amended and subsequently repealed Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/419/EEC, 86/280/EEC and amended Directive 2000/60/EC in relation to priority substances (European Union, 2008).

The list of 33 priority substances includes selected existing chemicals, plant protection products, biocides, metals, including cadmium, lead, mercury and nickel and their associated compounds and other groups like polycyclicaromatic hydrocarbons (PAH). In line with the list of priority substances, the Water Framework Directive aims at (European Parliament and Council, 2000):

- Progressive reduction of discharges, emissions and losses of priority substances to surface water bodies via limits and
- Cessation or phasing-out of discharges, emissions and losses of priority hazardous substances to surface water bodies by 2025.

The WFD establishes EU-wide limits for the substances in surface waters. These limits must be met by 2015 and discharges of priority hazardous substances will be checked in 2018 (Hebstreet, 2010). The list of priority substances is reviewed regularly using ecological monitoring data with the first review likely to take place at the end of the first River Basin Planning cycle in 2015 (Environment Agency, 2011b).

2.1.6.2 Current Status of the Waters in Western Wales District

According to Environment Agency (2009), there is a formal target of achieving 31% of surface waters in good ecological status or potential by 2015 across England and Wales.

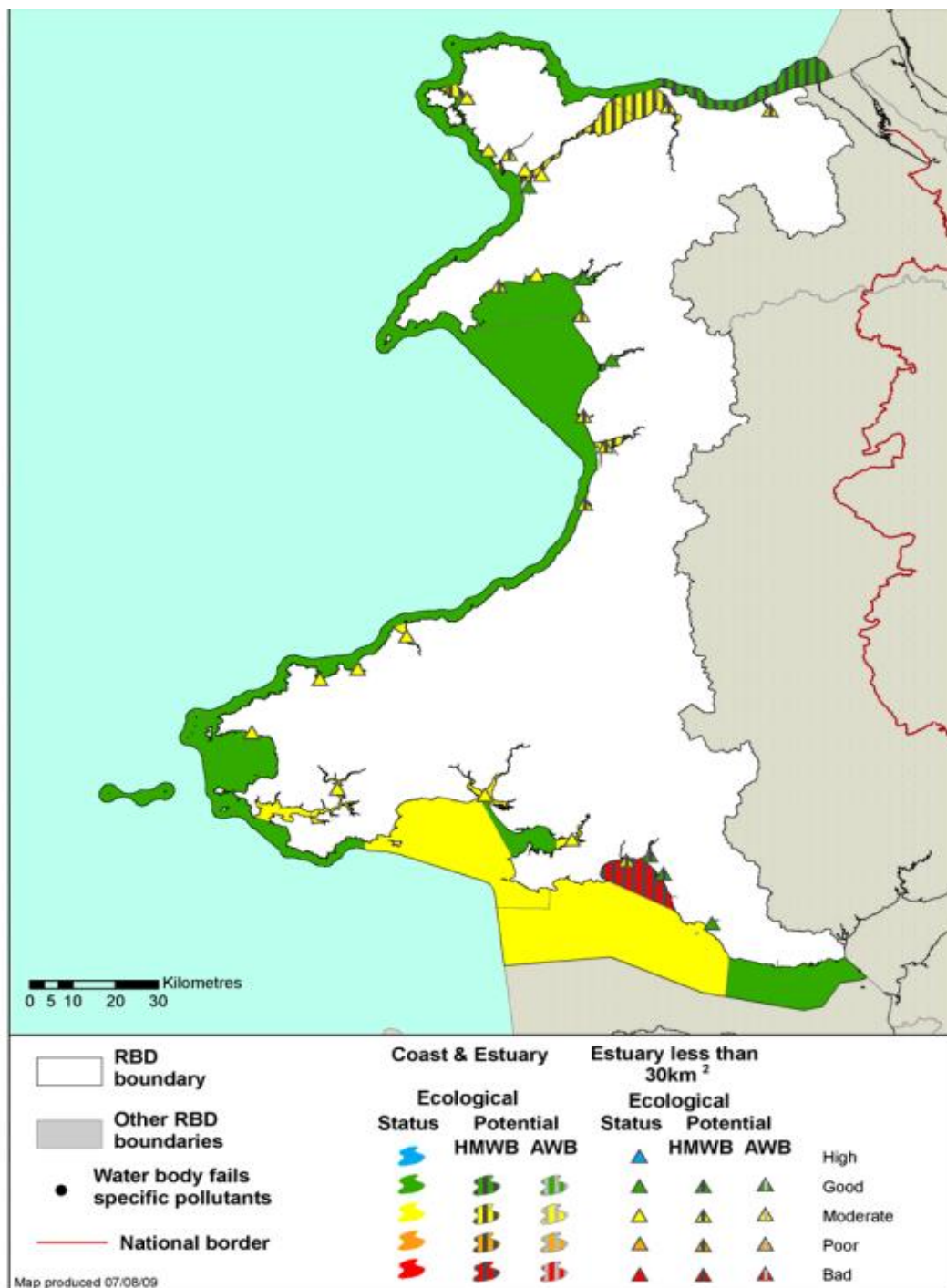


Figure 2.4 Ecological status or potential for estuarine and coastal waters (Environment Agency, 2009)

Within the Western Wales district, the ecological statuses of the lakes and ditches and the ecological status or potential for rivers, canals and surface water transfers bodies are all good or higher throughout Wales, as is the chemical statuses for all the water bodies (Environment Agency, 2009). This is not however the case for the ecological status of the surface water bodies as can be seen in Figure 2.4. The map for the predicted ecological status and potential for surface water bodies in 2015 reveals that the Swansea Bay area, where the Port Talbot Steelworks is located, is estimated to have a ‘bad’ ecological status and potential. The ecological status of all the Western Wales water bodies (Figure 2.4), apart from Swansea Bay is either moderate or good, which is likely to tighten the concent limit regime imposed by the Environment Agency on the industrial facilities located in the area.

2.2 Tata Steel Europe Port Talbot Steelworks

On the 2nd of April 2007 Corus Group was taken over by Tata Steel, established in 1907, which is Asia’s first and India’s largest private sector steel company. As well as the Corus plants in the UK and the Netherlands, Tata Steel has several steel plants across India and South-East Asia (Figure 2.5), with a manufacturing network of eight markets in South East Asia and Pacific Rim countries. In the UK, Tata Steel Europe is a major manufacturer with operations in Port Talbot, Scunthorpe, Newport, Corby, Redcar, York, Deeside, Wolverhampton and Rotherham. The takeover lifted Tata Steel to the list of top 10 steel producers in the World, with its production of approximately 31 MTPA (million tonnes per annum).



Figure 2.5 Tata Steel production plants (Corus World, 2007)

Port Talbot Integrated Steelworks is one of Tata Steel's main sites currently producing some 4.33 MTPA (in 2007) of crude steel (slab). The site covers an area of over a thousand hectares with 100 km of roads and has a deep-sea harbour for importing purposes. The site includes coke ovens, sinter plant, blast furnaces, basic oxygen steel-making (BOS) plant, continuous casting plant, hot strip mill, cold rolling mill and a continuous annealing line.

2.2.1 Port Talbot Steelworks Integrated Steel-making Process

Four routes are currently used for production of steel: The classic blast furnace/basic oxygen furnace route, direct scrap melting or electric arc furnace, smelting reduction and direct reduction (Figure 2.6). Within Port Talbot Steelworks the steel is produced using the integrated or so-called BOS production route, outlined on the left.

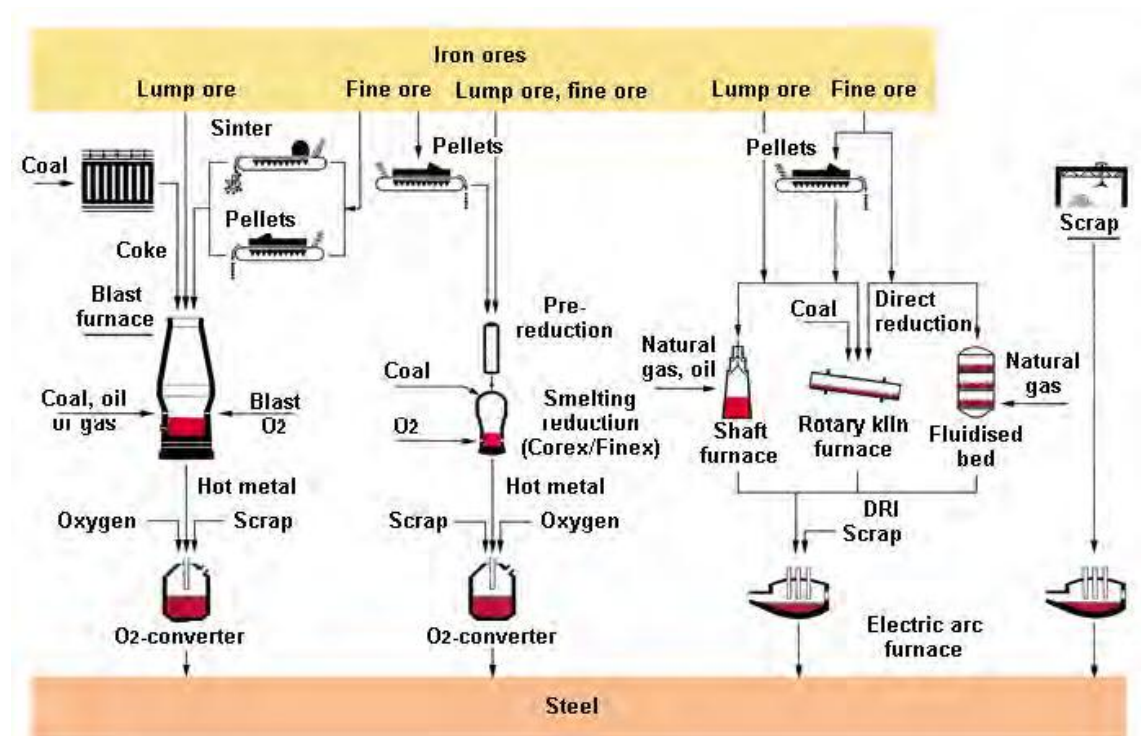


Figure 2.6 Crude steel production routes (EIPPCB, 2001a)

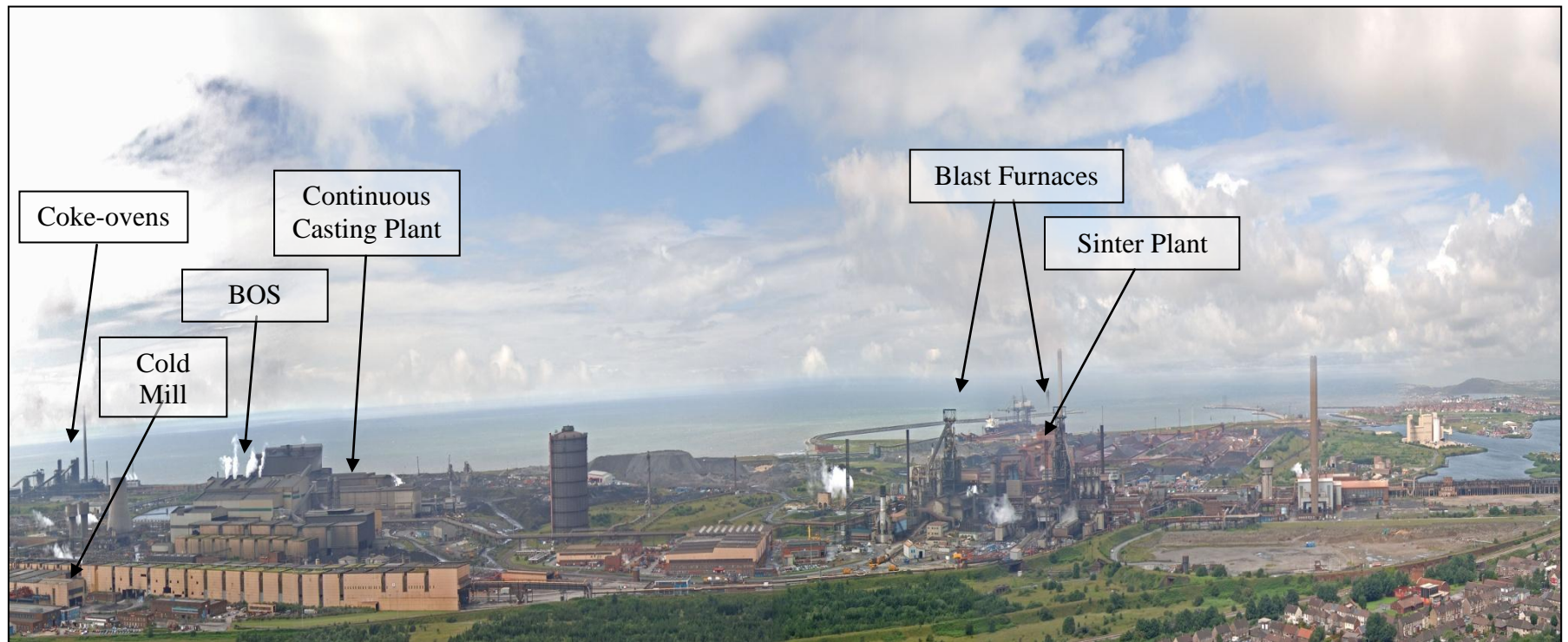


Figure 2.7 Aerial view of Port Talbot Steelworks

The World's steelworks can be categorised into three types of facilities:

- Integrated steelworks, which use ore, coke, limestone, energy and water to produce multiple products,
- Minimills, which use scrap steel to make limited types of products for multiple markets and
- Finishing mills, which use intermediate steel products to make products only for focused markets (Johnson, 2003).

Integrated steelworks are large industrial complexes, often located near coasts and covering areas of several square kilometres. Integrated steelworks are characterised by networks of interdependent material and energy flows between various production units, which can be divided into 4 different processing steps of iron-making, steel-making, rolling and finishing. In Port Talbot Steelworks, 8 industrial facilities are used for the production of high quality strip steel, namely coke-ovens, sinter plant, blast furnaces, BOS plant, continuous casting plant, hot mill, cold mill and continuous annealing plant. Most of these plants can be seen in the Figure 2.7 that outlines the 28 square kilometre-sized Port Talbot Steelworks.

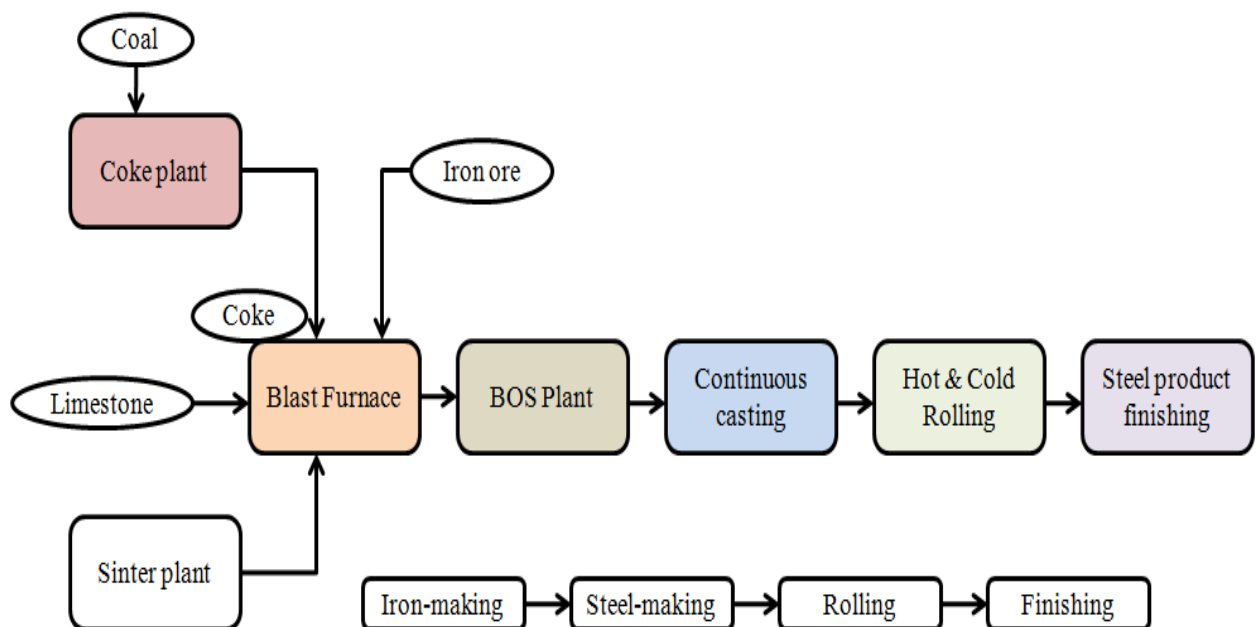


Figure 2.8 Flowchart of principal operations in integrated steelworks (Adapted from Yoon-Gih Ahn, 2006)

The purpose of iron-making process is to produce pig iron which, as can be seen in Figure 2.8, will be achieved through three separate steps of:

Coke-making – coal is converted into coke prior to being used in the blast furnace.

Sintering - the iron ore is roasted and agglomerated in preparation for converting to iron.

Blast furnace - the sintered ore, limestone, coke and other fuels are chemically reacted to reduce the iron ore to a crude metal called pig iron, which contains approximately 4% carbon (DTI, 2006). The blast furnace, where primary reduction of oxide ores takes place, is the main operational unit of the iron-making process. The coke-ovens and sinter plant merely serve a purpose of preparing the raw materials for use in the blast furnaces (Yoon-Gih Ahn, 2006).

As seen in Figure 2.8, the conversion of iron to crude steel slabs is carried out by two processes called basic oxygen steel making (BOS) and continuous casting:

BOS Plant - carbon level of iron is reduced to approximately 1% to create steel. This requires the use of high temperature furnaces and oxygen injection (DTI, 2006).

Continuous Casting – molten metal is continuously cast via a tundish into a water-cooled copper mould causing a thin shell to solidify. This ‘strand’ is then withdrawn through a set of guiding rolls and further cooled by spraying with a fine water mist. When the strand is fully solidified, it is cut into desired lengths or so called ‘slabs’.

A simplified schematic view of the main material inputs and outputs of each stage of the process route for iron- and steel-making can be seen in Figure 2.9.

In order to turn the crude slab steel into actual product ready for market, the slabs go through two further steps of rolling and finishing. In Port Talbot Steelworks two different kinds of rolling are carried out:

Hot Mill: the principal effects of hot rolling are the elimination of the cast ingot structure defects and obtaining the size, shape and metallurgical properties required for further processing (EIPPC, 2001b)

Cold Mill: further rolling of the strip to create thin, strong and ductile strip with a surface capable of the highest quality of paint finish (Corus Strip Products UK, 2009).

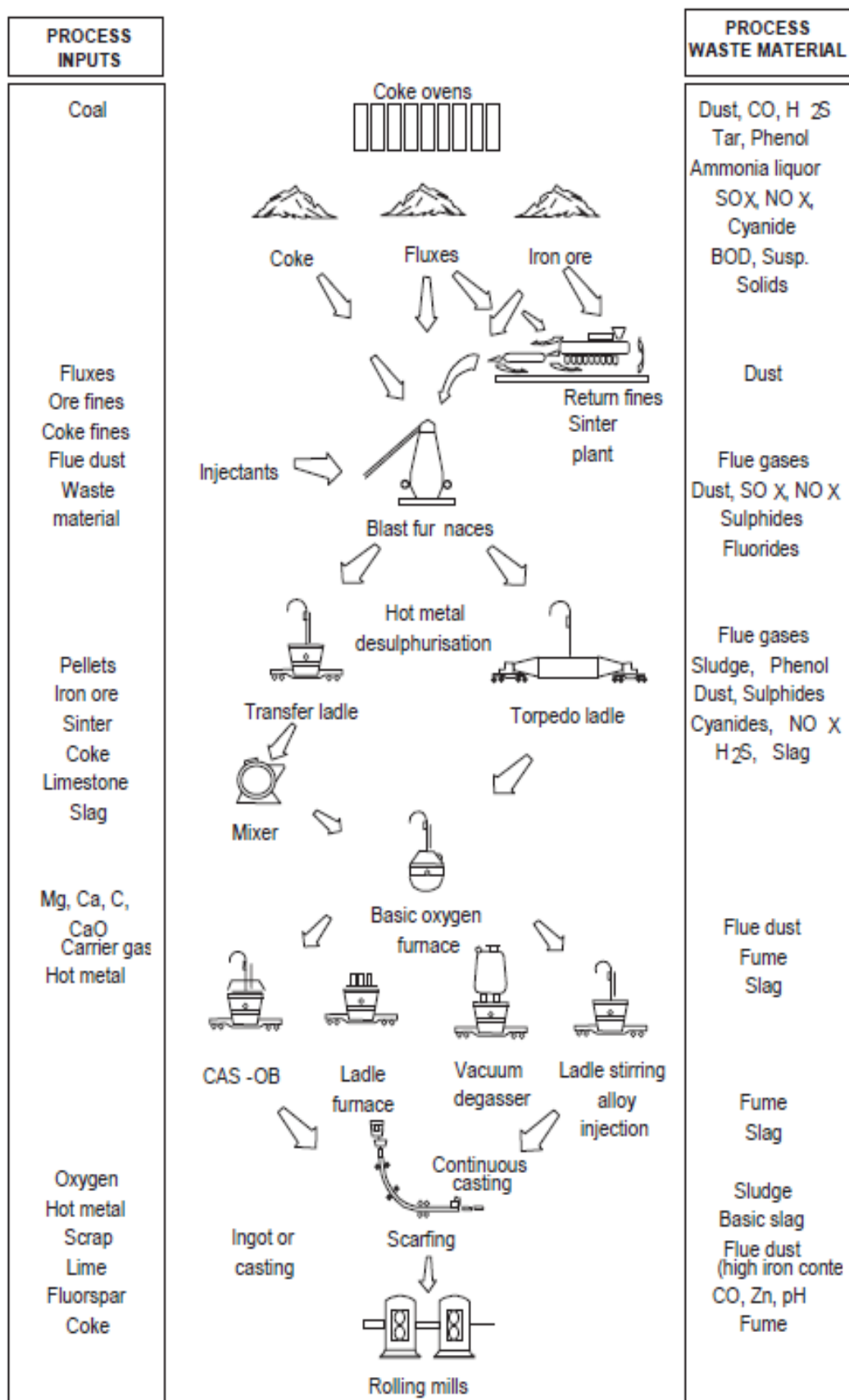


Figure 2.9 Process flow for iron and steelmaking (Environment Agency, 2004)

The last step in the integrated steelmaking is finishing, which in the Port Talbot Steelworks includes a Continuous Annealing Plant (CAPL):

CAPL : a heat treatment of the steel at a designated temperature, followed by cooling in order to increase ductility of the steel. Different annealing processes use different annealing temperatures, holding times and cooling rates to achieve the final microstructure and properties required (Steeluniversity Website).

2.3 Water in Integrated Steelworks

All steelworks, especially integrated ones, use great amounts of water for production of steel, whether it's long, flat or stainless steel that is being produced, with considerable quantities being required for equipment cooling, material processing and waste treatment amongst other things. The water management in integrated steelworks primarily depends on the local conditions and above all on the availability of fresh water and on legal requirements.

There are huge differences in water consumption between different integrated steelworks in the World. The main reason for this is the amount of once-through cooling systems within the different production units of the integrated steelworks. As an example, if many once-through cooling systems are in place within the steelworks, the water consumption can exceed 250 m³/t steel, whereas in sites with very little fresh water available, the cooling water is recycled in a closed circuit cooling system and combined with other water saving measures, the specific water consumption can be less than 5 m³/t steel (EIPPCB, 2001a). Average water consumption figures within steelworks are approximately 30 m³/t of steel (Suvio et al., 2010a) as will be explained later in Chapter 4.

Although water use patterns vary considerably between different steelworks, freshwater is an essential input for the production of crude steel and also brackish and sea water is used. Most of the water is used for once-through cooling purposes. According to Worldsteel (2011), the primary iron- and steelmaking processes require raw materials to be heated beyond the melting point of iron, whereas the hot rolling operations require heating to enable certain metallurgical equipment. The equipments used in these heat

processes are often protected by a combination of refractory lining or equipment shells and water-cooling. In most cases, the water used for cooling purposes is cooled and treated, either for reuse within the plant or in order to enable return to its original source.

Water is also used for (Johnson, 2003):

- Material conditioning (water is used for dust control in sinter feeds, slurring or quenching dust and slag in blast furnaces, mill scale removal in hot rolling operations, solvent for acid in pickling operations, or for rinsing in other rolling operations),
- Air pollution control (primary operations, particularly in integrated mills, use water in wet scrubbers for air pollution abatement and
- Acid control in pickling operations and for wet scrubbers in coating operations that have caustic washing operations.

2.3.1 Effluent from Steelworks

When great amounts of water are being used in production, great amounts of effluent water are born with an average effluent production per tonne of steel being 25 m³ (Suvio et al., 2010a). Due to ever intensifying water scarcity and evolution of water-related legislation, it's crucial to manage the treatment and disposal of this waste water properly. One of the actions steelworks are taking to manage their effluent is monitoring the quality and quantity of their water emissions to prevent compliance limits being exceeded and taking corrective actions if they are exceeded (worldsteel, 2008).

Under present and forthcoming EU-wide legislative demands, every production unit within European-based integrated steelworks ought to have their own water treatment plants with primary treatment processes and some facilities with secondary treatment processes. The level of the treatment ultimately decides whether the treated wastewater can be recycled back for reuse, or whether it needs to be discharged.

The two most complex type of effluent arisen from the operation of the steelworks two pyrometallurgical processes; coke-oven and blast furnaces. The effluent arisen in both cases is gas cleaning effluent, which contains contaminants released and formed during the operations of the pyro processes. The effluent arisen in these processes is further explained in depth Chapter 3.

The individual facilities asides, large volumes of generic low metal-concentration effluent containing mainly low concentrations of metals and other suspended solids (SS) is arisen during the operation of steelworks, including effluent from:

- Indirect cooling, including BF hearth cooling, etc,
- Direct heat treatment, where water is applied straight to the product e.g. in rolling to achieve right metallurgical properties,
- Equipment cooling and
- Final effluent, which consists of a combination of effluents from the different facilities that are mixed together for discharge or final effluent treatment.

This type of effluent forms in many cases >95% of the total wastewater arisen at the steelworks and possess great potential if sufficiently treated and reused back to the process.

2.3.2 Sustainable Water Management (SWM) in Steelworks

Steelworks are located in many regions of the world and the issues regarding freshwater are equally diverse; in some cases the availability of water is the issue, while in other cases the quality of water released back into natural water systems is the prevailing issue. The global steel industry is able to meet these challenges by providing solutions that at times even result in an increase in the quantity and quality of the locally available freshwater supply. In situations where there is a need for steel production in areas of limited freshwater availability, SWM efforts have made it possible to maintain freshwater intake at a relatively low level, with some facilities achieving a freshwater recirculation rate of nearly 100%, therefore creating a 'zero-effluent site' (Johnson, 2003). SWM plays a critical role in the viability of steel plants, especially in regions of

water scarcity, while increasing demands for water resources will make continued recycling of water a business imperative in the steel industry.

Steelworks have evolved over time, together with their water and effluent networks. This often leads to complex pipe networks, pre and effluent treatment systems and quality testing in order to ensure legal compliance. Sometimes there is no clear picture of the types or volumes of water running in some of the pipes. This should be the starting point of sustainable water and effluent management and can be solved by carrying out a pipe inventory and installing a comprehensive metering, monitoring and targeting system, which can help to manage the effluent and water systems properly and even reduce water consumption and effluent discharge volumes considerably.

One of the technical challenges standing in the way of SWM of the steel industry includes the choice of final effluent treatment. In many cases a basic chemical sediment/clarification system combined with flocculant treatment can give high enough effluent water quality to meet legislative effluent discharge targets, but sludge born as a side product of this type of treatment is voluminous, settles slowly and can prove hard to handle. This leads to the need for additional sludge handling by either filter-pressing or centrifuges and raised landfilling costs. The problem with the sludge can be overcome by using sludge-reducing water treatment, such as High Density Sludge (HDS) process, which was studied as a part of the project described in the thesis in Chapter 6.

One prevailing technology, which has been used increasingly in the recent years in steelworks are membrane processes. Membrane technologies come in various different formats, including ultrafiltration (UF), reverse osmosis (RO), electrodialysis (ED) and electrodialysis reversal (EDR). Membrane technologies can potentially provide a solution to practically any water treatment problem, but can't unfortunately be used alone as the effluent water entering any membrane process treatment should be relatively free from colloidal particulates, such as silt and iron and manganese oxides (GE, 2007). Unfortunately the need for combined treatment for large volumes of final effluent treatment can prove to be expensive and beyond the budgets of some steelworks.

2.4 Introduction into Industrial Effluent Treatment

Effluents can be characterised according to their physical, chemical, and microbiological characteristics and almost all of these characteristics can act as pollutants. Within Steelworks the unwanted effluent characteristics can include dissolved or suspended solids, metals, nonmetal ions, heightened biochemical (BOD) and chemical oxygen demand (COD), organic carbon, oil and grease and deviated pH and temperature. Looking beyond the unwanted characteristics present in steelworks effluent, Eckenfelder (2000) lists several undesirable wastewater constituents that may have to be removed before discharging the water. These include:

- Soluble organics,
- Suspended solids,
- Priority pollutants such as phenol and other organics,
- Toxic organics,
- Metals,
- Cyanide,
- Nitrogen and phosphorus,
- Refractory substances resistant to biodegradation,
- Oil and gloating material,
- Colour,
- Turbidity,
- Volatile materials and
- Aquatic toxicity.

In terms of effluent treatment, this study particularly concentrates in the operation and efficiency of the current conventional precipitation effluent treatment system in place at the Tata Port Talbot Steelworks as explained in Chapter 3, and further studies the HDS Sludge process that would provide a very beneficial upgrade the existing system as explained in Chapter 6. However, in order to get an understanding of what types of effluent treatment methods are available for industry, a short introduction to existing techniques will be provided here.

2.4.1 Treatment technologies

Multiple effluent treatment methods have been developed for treatment of different unwanted characteristics and constituents in the effluent water. The choice of water treatment technique depends on the quality and variability of the effluent source and treatment objectives, which may vary from one industrial facility and process to another. Overall, all the effluent treatment technologies can be divided into 3 different groups of pre and primary, secondary and tertiary treatment, depending on where within the treatment process chain the technology is used.

2.4.1.1 Pre- and Primary Treatment

A wastewater treatment plant that only incorporates sedimentation as the major treatment operation is often referred to as a primary treatment plant. The objective of pre- and primary treatment is to render the wastewater suitable for subsequent treatment. Pre and Primary treatment tackles settleable and floatable solids and its main aim is to reduce the suspended solids content of the water (Fish, 1992). Sometimes pre- and primary treatment alone is used for effluent treatment. A simplified process flow of most common pre- and primary treatment technologies are shown in Figure 2.10.

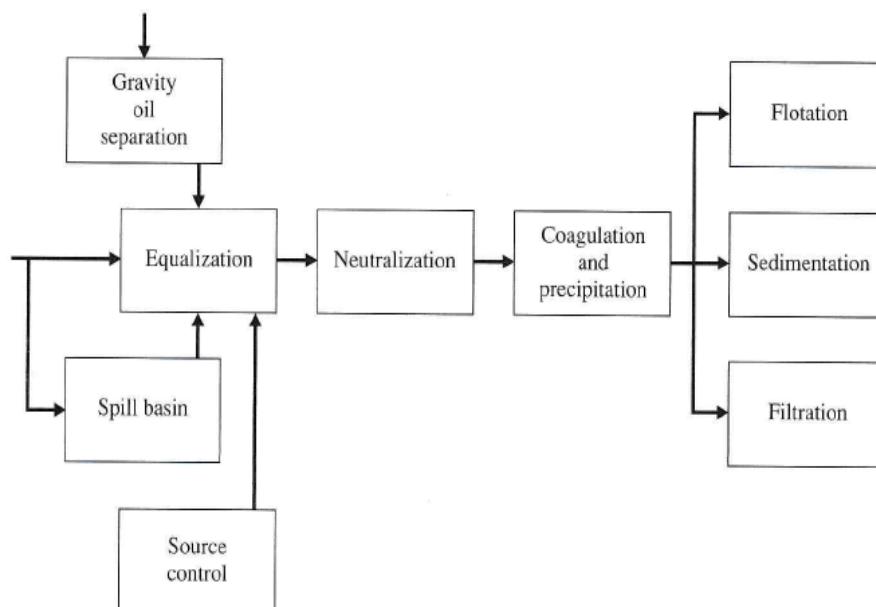


Figure 2.10 Pretreatment technologies (Eckenfelder, 2000)

2.4.1.2 Secondary Treatment

After the pre and primary treatment, effluent can be either discharged or further processed in a secondary treatment or tertiary treatment step. The secondary treatment step entails provision of biological treatment and it is used when there is a high biological load within the effluent to be treated. The purpose of the secondary treatment is to reduce BOD by replicating micro-organisms-mediated degradation of organic matter. Manahan (2005) states that in order to achieve this, waste is oxidised biologically under conditions controlled for optimum bacterial growth. Within steelworks biological treatment is commonly applied for coke-oven gas washing effluent treatment. Generally only pretreatment, and in some cases tertiary treatment technologies are applied to steelworks metal containing effluents.

2.4.1.3 Tertiary or Advanced Treatment

More advanced effluent treatment techniques are also called tertiary effluent treatment. Advanced treatments systems often include advanced filtration (e.g. sand filters), adsorption, ion-exchange or membrane technology. The reverse osmosis (RO) is part of membrane treatment technologies and is most suitable for the removal of different contaminants. When it comes to dissolved metals, precipitation is however, often the cheapest option and, especially with dissolved metals, often the best.

2.4.1.4 Low Metal-Concentration Effluent Treatment

Wastewater born in steelworks has high volumes with low concentrations of dissolved metals. Several methods have been developed for the removal of metals from solution, which include chemical precipitation and oxidation, which are often more efficient by using further coagulation or flocculation that improve the sedimentation of the sludge arisen when metals ‘drop’ out of solution. Other treatments that have been successfully used for the treatment of metal-containing effluents include tertiary treatment methods, such as flotation, filtration, adsorption, ion exchange and membrane technology. The choice of technology often depends on the required level of metal removal. Tertiary treatment can achieve very low metal concentrations, but often has higher capital costs

and requires a pretreatment step or operational costs of the treatment will rise significantly.

The research project that forms the basis for this thesis concentrated especially on treating low metal-concentration effluent with two individual effluent treatment technologies. The first of these is being chemical precipitation, where chemical reagents often including a hydroxyl anion (OH^-) are used to raise the pH react with the metal cations, therefore creating conditions, where metals become insoluble as explained in more detail in Chapter 5. Chemical precipitation is often combined with a flocculent sedimentation, which by exposing the water to quiescent conditions, will allow settleable solids to be removed by the force of gravity. Chemical precipitation and settlement system, using type II (flocculent) settling (Gray, 2005) is the treatment currently being used for the final effluent treatment plant of Port Talbot Steelworks.

The problem associated with chemical precipitation followed by sedimentation is that the voluminous sludge accumulated in the tanks needs to be often dewatered and disposed via landfill (Droste, 1997). It is possible to dewater sludge by using simple concrete dewatering bunds or similar but according to Eckendfelder (2000) common dewatering techniques used for metal-containing sludge include gravity thickening, flotation, filtration (including filter-presses, etc.), drying and centrifugation. Following dewatering sludge is often sent to land disposal or incineration.

The main treatment that has been the focus of this study is High Density Sludge (HDS) process, which is a modified precipitation process, where sludge that accumulated in the process is recycled back to the beginning of the treatment process. HDS specifically targets the volumes of sludge being born as a side-product of the treatment, by creating sludge that is easy to handle, settles fast, requires little or no dewatering and has low volumes.

2.5 Conclusion

Water related issues have been under a great deal of focus in the UK during recent years and the Water Framework Directive (WFD) 2000/60/EC is set to overhaul the

management of the water environment within the EU, by requiring all inland and coastal waters to reach "good status" by 2015, placing pressure on large industrial facilities, including steelworks.

Tata Steel Port Talbot Integrated Steelworks produces some 4.33 MTPA (in 2007) of crude steel (slab) and is a major user of water with its 8 production facilities and supporting functions.

Freshwater is essential for the production of steel and it is used in several processes within a steelworks. The most common use for water is cooling, which can be indirectly and most often used for equipment or gas cleaning or directly to the product to enable certain metallurgical characteristics. The most complex effluents arisen from the steelworks operation include coke-oven and blast furnace effluents, in both cases as a consequence of gas cleaning following a pyro process.

Sustainable water management (SWM) is important within steelworks and SWM efforts have enabled some facilities to achieve freshwater recirculation rates of nearly 100%, therefore creating a 'zero-effluent site'.

Effluents can be characterised according to their physical, chemical and microbiological characteristics, which can all act as pollutants. Several effluent treatment techniques are available for industrial effluent treatment and they are commonly divided into pre or primary, secondary and tertiary treatment.

3 CRITICAL ANALYSIS OF THE PORT TALBOT STEELWORKS WATER SYSTEMS

3.1 Introduction

Water is an essential resource for the iron and steel making processes, with considerable quantities being required for product and equipment cooling, material processing and waste treatment, amongst other things. Water constraints in Port Talbot Steelworks are already putting pressure on production with any new production process adding further constraint. Port Talbot Steelworks have recently experienced a number of periods of water shortages including the summers of 1984, 1995, 2004 (Energy Department, 2005) and the latest in 2009, posing a threat to the satisfactory operation of the Steelworks' production facilities. The Port Talbot site is facing problems with water supply as the water abstraction sources currently used are fully exploited and past summer droughts have resulted in reduced water volumes and quality. Further, ever intensifying climate change will be placing extra pressure on the existing water sources with increased temperatures and therefore decreased water availability and quality.

Within the Port Talbot Steelworks, the Energy Operations Department oversees the supply and distribution networks, treatment of water and effluent outside the borders of the individual facilities. The effluent treatment activities under the Energy Operations Department, although overseen by Energy Operations Department, are carried out by Nalco Chemical Company. The responsibility between a specific facility and the Energy Operations Facility changes when the water enters or leaves the perimeter of a specific facility prior to it crossing the border between where the facility starts and the responsibility of the Energy Operations Department ends.

In the past, water has been perceived as an abundant resource with very low direct cost in the Port Talbot Steelworks. Until this work, no extensive studies on water supply systems, amount of water used and amount of effluent water produced have been carried out. Some studies relating to the works' effluent water systems have been carried out. The most important include the Engineering Doctorate studies of Swindley (1999) on how to control the effluent arising from the steel production on the plant and Jones

(2005) on how to recover metal from wastewater. These studies concentrated on effluent water but despite the above studies, there is a continuing need to improve the effluent water quality due to ever tightening legislative requirements, including the Water Framework Directive (WFD), which will be placing extra pressure on businesses to remove metals, particularly heavy metals from production-born effluent water prior to discharge.

3.2 Water Supply Systems

At Port Talbot Steelworks, water supply and distribution systems have evolved in parallel with the growth of the processing facilities, increasing quality requirements and progressive introduction of waste treatment and pollution control systems.

The Energy Operations Department is in charge of the abstraction points and delivery of the water within the overall site. This responsibility passes over to the specific production facilities once the water supply crosses the border of the facility.

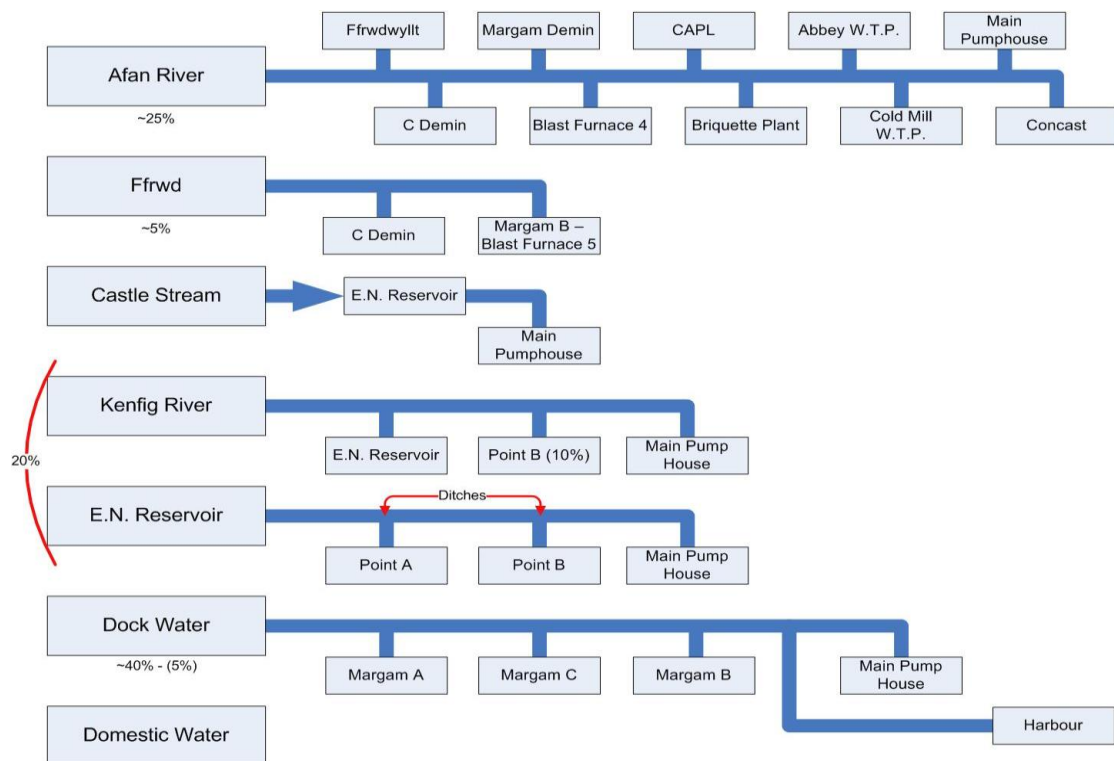


Figure 3.1 Water Abstraction Points at Tata Port Talbot Steelworks (Water Experts Team, 2006)

As can be seen in Figure 3.1, beside domestic water, the water used by the Port Talbot works comes from 6 different sources: The river Afan is used without pre-treatment in several processes and is also further pre-treated to soft and demineralised water at the several water treatment plants within the site prior to use in processes requiring higher water quality. River Afan also supplies water to the Dock (Figure 3.2) and this, in turn, is used as cooling water for the western part of the site along with the Ffrwdwyllt river abstraction. The water at the Dock is brackish as at times of low water flows, the Dock is topped-up by sea water.

The Castle Stream and Kenfig River are used to supply water to Eglwys Nunydd Reservoir (Figure 3.2), which feeds the Main Pump House with the majority of the process water used within the site. Most of the water pumped to the Main Pump House is further pumped to the Works Reservoir and becomes service water for the Steelworks processes.

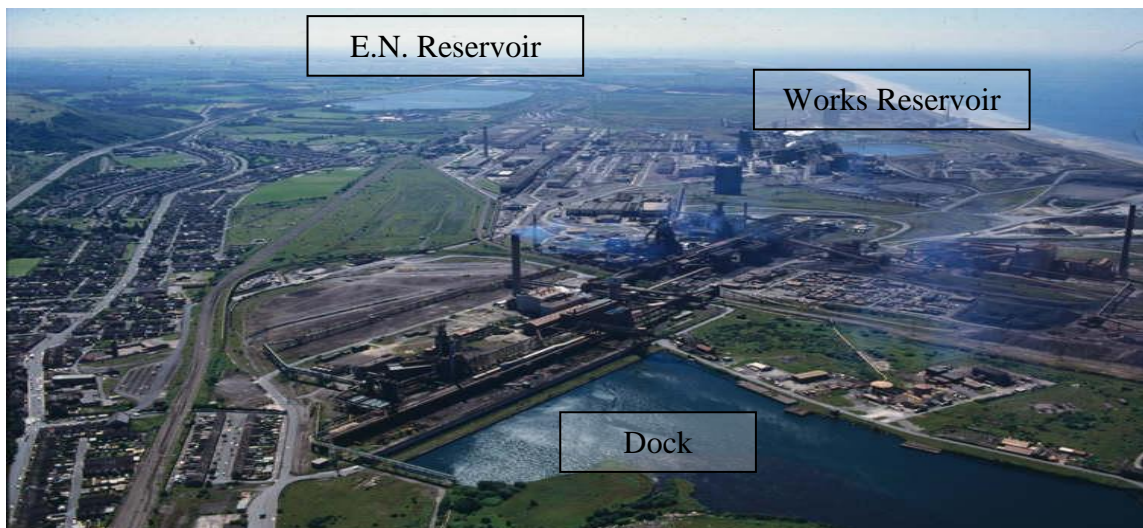


Figure 3.2 Main water reservoirs at the Port Talbot Steelworks

3.2.1 Water Supply Flows

Steel making processes use considerable quantities of water and Port Talbot Steelworks solely consumes over 400 million litres of water per day, totalling some $146,000,000 \text{ m}^3$ a year. In 2007² $145,020,000 \text{ m}^3$ of the supply water came through abstraction from

² Year 2007, because the Port Talbot data used for Chapter 4 is based on that specific year and prior to 2010 it was the last year when the Port Talbot Steelworks was operating in full capacity

natural water sources and some 800,000 m³ of potable water was provided by Welsh Water.

Tata Strip Products UK Port Talbot Steelworks gets most of its water supply through natural sources, which have abstraction license limits set by the Environment Agency. Specific flows for the different abstraction points, together with the limits set by the Environment Agency, can be seen in Table 3.1. As can be seen, the biggest water source is the Docks with a >88% fraction of the use. The water abstracted from the Docks is brackish and is used mainly for the Blast Furnace hearth cooling. Out of the freshwater sources the Afan River is the largest with nearly a 6% share of all water abstracted and it is the source with best quality.

Table 3.1 Abstraction figures and limits for 2007 with % abstracted and fraction of the use

Abstraction Point	Abstracted (m³/year)	Limit (m³/year)	Abstracted %	Fraction of use %
Afan	8,315,822	14,913,900	56	5.88
Ffrwdwyllt	1,545,376	2,270,000	68	1.09
Castle Stream + Kenfig	2,708,436	11,807,000	23	1.91
Docks	124,893,865	206,343,00	62	88.30
Point B	3,985,537	1,225,800	325	2.82

The abstraction volumes generally stay within the abstraction limits, besides Point B, where the flows can't be controlled and abstraction is imperative, especially in times of high rainfall, in order not to flood the moors located next to the Steelworks.

All the natural water sources are subject to seasonal and climatic variation, meaning higher water levels in the winter and spring seasons associated with good water quality, neutral pH, low chlorides and low conductivity levels and the opposite in summer and autumn (Energy Department, 2005).

3.2.2 Water Mass Balance

‘The amount of water entering a site equals the amount of water leaving the site’. This simple observation is called ‘water mass balance’. Quantifying the components making up a site's water mass balance is a powerful technique for identifying how much water

is wasted in the process (Envirowise, 2005). In order to create an overall picture of present water usage and consumption levels, wastewater created against the steel produced, together with water wasted within the processes, a high-level water mass balance model (Figure 3.2) with water related input and output was built. The year 2007 was specifically selected as it represents the last year with full production capacity prior to the economic downturn.

The incoming water balance was attained from:

1. Raw water input from rivers, streams and the reservoir (metered),
2. Raw water from the Dock (metered) and
3. Flow estimates relying on pumping capacity for the remaining water sources.

The outputs were attained from:

1. Balance of the cooling water sent back to the Docks (careful estimation by energy department),
2. Wastewater from the works to the Long Sea Outfall (metered) and
3. Careful estimation of effluent pumped to the final effluent treatment plant (Nautilus).

As can be seen in Figure 3.3, out of the total raw water abstracted, some 125,000,000 m³ is abstracted from the Docks. Nearly 10,000,000 m³ of this disappears as evaporation through processes, while the remaining ~115,000,000 m³ is returned back to the Dock for re-use. The ~10,000,000 m³ of water consumed within the process creates ~33% portion of the total 30,020,000 m³ of water that is consumed by the Steelworks annually. Another important raw water abstraction source are the rivers Ffrwdwyllt and Afan, which total 9,860,000 m³ of water abstraction annually and create a portion of 33% of water consumed annually.

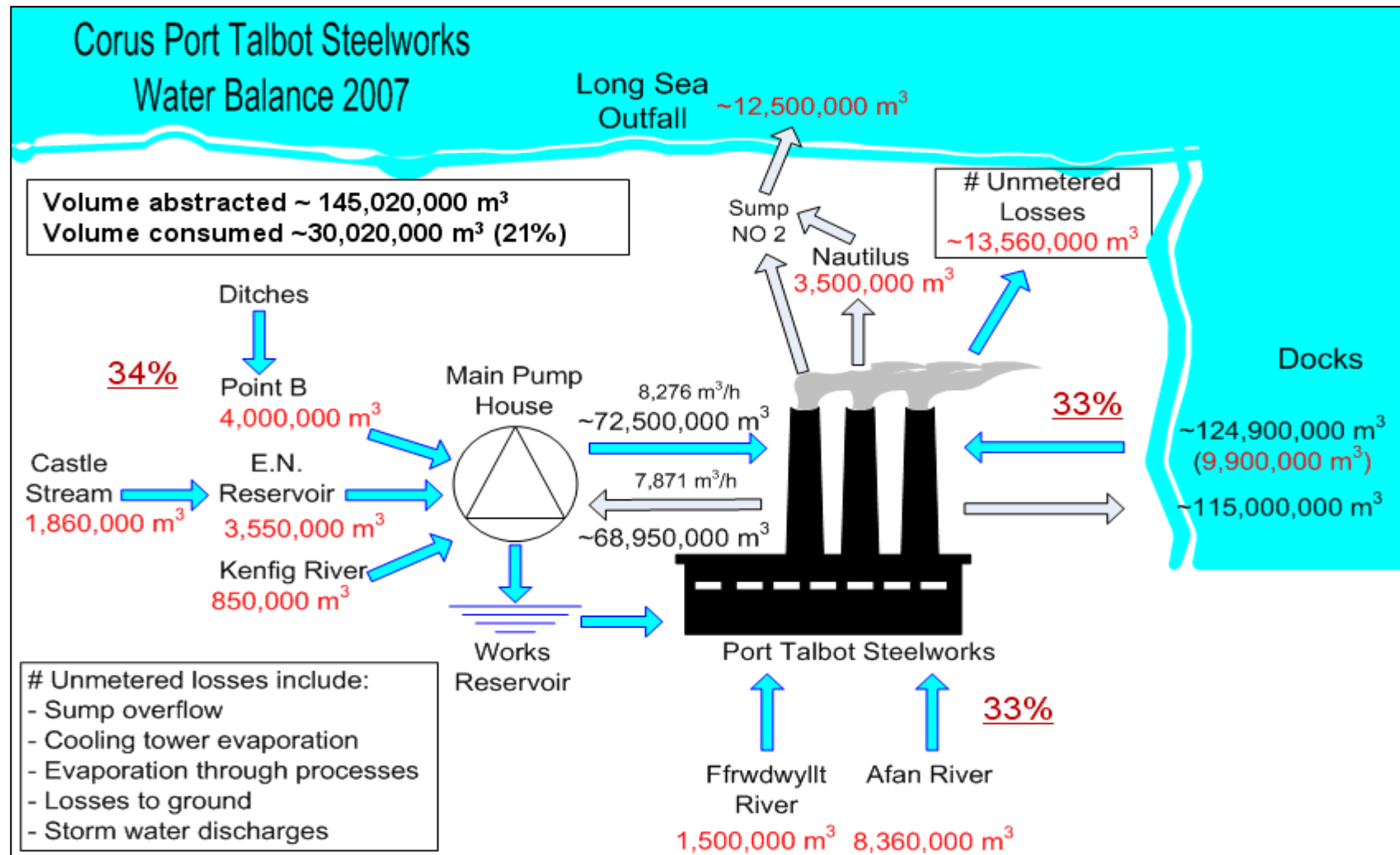


Figure 3.3 Port Talbot water mass balance (2007)

Consumption of large volumes of water leads to a large volume of effluent being generated during operation. Figure 3.6 highlights that some 12,500,000 m³ (2007) effluent or 41% out of the consumption is discharged annually via the Long Sea Outfall. Out of this volume around 1/3 is treated by the Nautilus final effluent treatment plant, the rest is pumped straight to the final effluent receiving Sump No 2, prior to being discharged to the sea via the Long Sea Outfall. On top of the effluent discharges, there is around 13,560,000 m³ of water lost per annum through unmetered losses, including sump overflow, cooling tower evaporation, losses to ground, storm water discharges and evaporation through processes.

The so called service water used within the site enters the site through the Main Pump House (MPH), where the water used as a top-up for the recirculating cooling systems is pumped from several abstraction points, including the Castle Stream from where some 1,860,000 m³ flows to Eglwys Nynydd (E.N) Reservoir, from which an additional 3,550,000 m³ is added to the abstraction. This combined abstraction volume of 5,410,000 m³ is then pumped to the MPH to be used as service water within the site. Another source for the MPH service water is ditches, from where the raw water flows to Point B and is pumped to the Main Pump House. The final abstraction point for the MPH service water is the Kenfig River, which provides the remaining 850,000 m³ of the total 10,260,000 m³ service water arriving to the MPH via abstraction. The service water abstraction totals the remaining 34% of the total water consumed by Steelworks annually.

3.2.3 Supply Water Quality and Pretreatment

As mentioned earlier, most of the water used within the site is so called service water. This water is used directly from the Works Reservoir, where it is stored prior to use. A typical analysis of the service water can be seen in Table 3.2.

The service water system is the most complicated individual water system within the steelworks providing water to most of the facilities, including production facilities via the Main Pump House as shown in Figure 3.4.

Table 3.2 Typical analysis of works reservoir water (Energy Department, 2005)

Works Reservoir Water Analysis	
Total Alkalinity	80 mg/L as CaCO ₃
Calcium Hardness	95 mg/L as CaCO ₃
Total Iron (Fe)	2 ppm
Soluble Iron	0.1 ppm ³
Suspended Solids (SS)	12 ppm
Chloride	45 ppm
pH	7.6
Conductivity	380 µS/cm
Oil	10 ppm

High re-circulation of the water and the increasing chloride content of the raw water from the rivers have increased the overall chloride levels in the Works Reservoir and therefore the service water. During drought periods, chloride levels are especially high which can cause problems in several processes, especially via increased corrosion rates in stainless steel equipment. Generally, a water supply with chloride levels of less than 200 ppm is required to prevent equipment damage. However, the typical summer means chloride levels at the Service Water system are around 400 ppm (Energy Department, 2002).

Next to service water, an additional 5 raw water types are used within the Port Talbot Steelworks, including: River Afan, Ffrwdwyllt River, River Kenfig, Eglwys Nunydd Reservoir and the Docks water. The biggest individual raw water source is the Afan River, which flows down Cwm Afan from the Rhigos mountain to the area of Port Talbot's Docks. There is a weir upstream of the river mouth and the abstraction point is upstream of the weir.

A typical analysis of Afan River water is (Energy Department, 2003):

- pH 7.2-8.3
- Chloride 15-30 ppm
- Conductivity 80-300 µS/cm
- Suspended solids 50-170 ppm

³ ppm = mg/l at standard temperature and pressure density (kg/L)

Port Talbot Works SERVICE WATER System

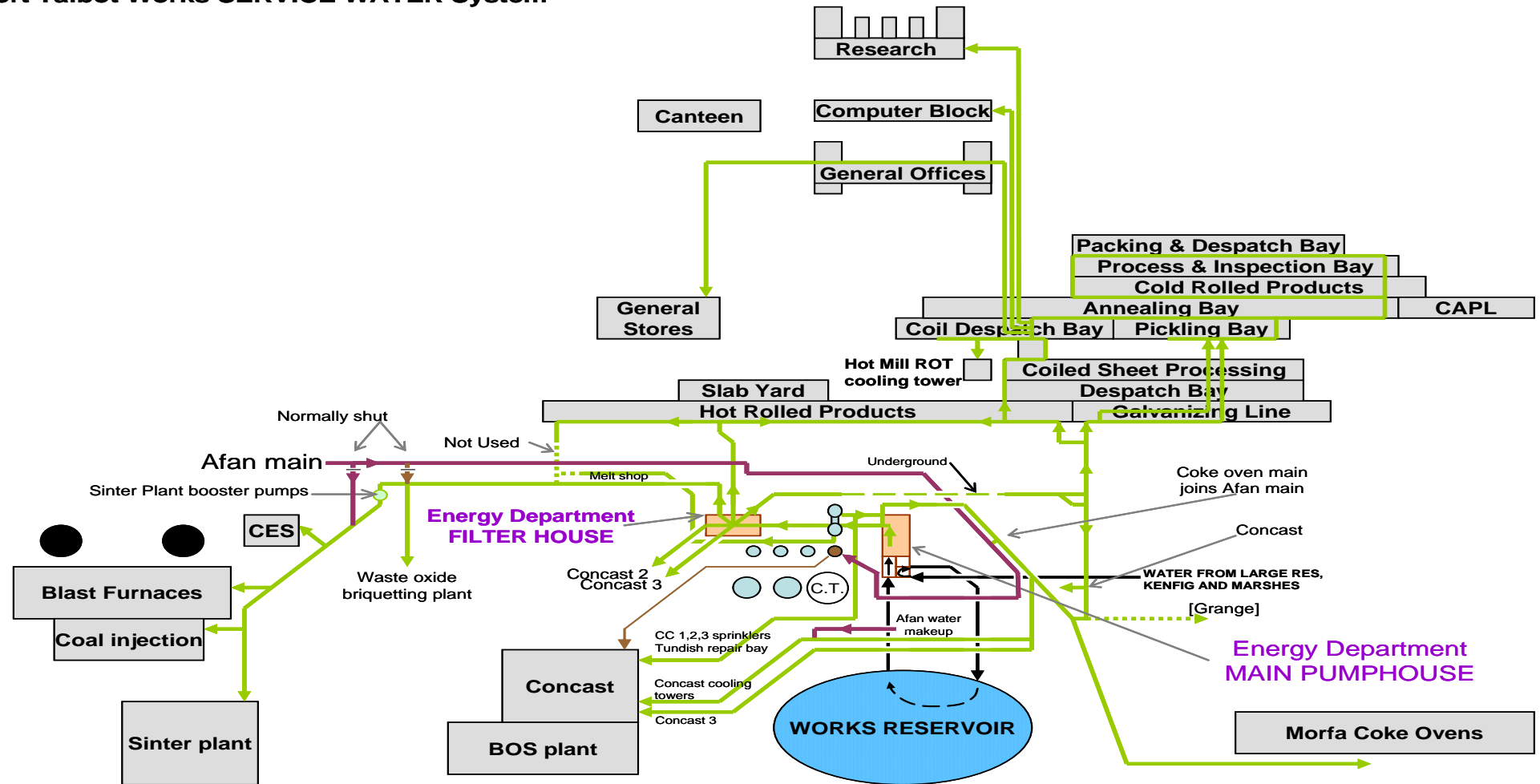


Figure 3.4 Port Talbot Service Water Systems (Morris, 2009)

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The Afan River is also the main supplier to all of the Steelworks pretreatment plants, which include:

1. Abbey WTP (demin and soft)
2. Cold Mill Lime Water Treatment Plant
3. Margam C Demin Plant
4. Margam Demin Plant

Ffrwdwyllt River water is abstracted by a pump house at Taibach and is pumped to a system linked closely to the River Afan distribution system. Next to being used for the No 4 Blast Furnace cooling system, Ffrwdwyllt River water is used as an emergency top-up to the de-mineralising and soft water treatment plants. Typical analysis of Ffrwdwyllt River water is (Energy Department, 2003):

- pH 7.5-9.2 (normally 7.5-8.3. High pH in drought conditions)
- Chloride 20-50 ppm and
- Conductivity 100-350 $\mu\text{S}/\text{cm}$.

River Kenfig, Eglwys Nunydd and Ditch overflow all end up at the Works Reservoir, from where they are pumped to the site as service water, but it should be noted, that a typical analysis of Kenfig River is (Energy Department, 2003):

- pH 7.3-7.5
- Chloride <20 ppm and
- Conductivity <100 $\mu\text{S}/\text{cm}$.

However, in periods of drought the Kenfig River flow is reduced and the quality deteriorates. Also, the Castle Stream has large seasonal variations in its flow and chemical quality. As with Kenfig River, the winter months see high quality water with high flow and summer can provide a struggle to have any flow at all.

As mentioned, the Docks water sometimes contains high levels of contaminants and this together with high water temperatures and levels can provide a real struggle especially during summer months. Dock water is also brackish and leads to corrosion in the systems as, at times of lowered Afan River flows, the Dock is topped-up from the sea. This happened for the last time in summer 2009. Typical analysis of Dock water is:

- pH 7.6
- Chloride 110 ppm and
- Conductivity 486 $\mu\text{S}/\text{cm}$.

The quality of water deteriorates substantially in dry conditions, when typical analysis of Dock water is:

- pH 7.6
- Chloride 1060 ppm and
- Conductivity 2840 $\mu\text{S}/\text{cm}$.

3.3 Effluent Water Systems

The majority of the wastewater from the various processes within the steelworks are collected in local satellite sumps and pumped to a central collection sump known as Sump No. 2, where the various wastewaters are mixed together before being discharged to sea through a 3 km Long Sea Outfall. Alternatively, effluent is treated at Nautilus prior to being pumped to Sump No. 2. Figure 3.5 shows a simplified diagram of the wastewater system layout.

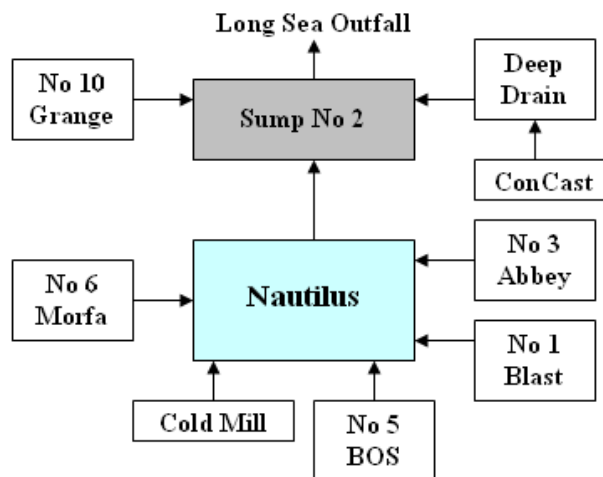


Figure 3.5 Tata Port Talbot Steelworks Wastewater System Layout

The ‘No. 5 Sump’ collects the process water from the Basic Oxygen Steel-Making (BOS) process. The No. 6 and 10 sumps are connected to the sites of the Coke Ovens and are further used for process water and drainage from roads and stockpiles in this

area. The Cold Mill Sump contains effluent produced by the Cold Mill Pickling Lines, where the steel coils are taken through acid baths to remove impurities prior to coatings. The No. 1 Sump is collecting effluent from the west side of the plant including Blast Furnaces. The No. 3, 'Abbey Sump', is collecting the drainage from the moors and overflows from various sumps. The main wastewater sources together with their collecting sumps are detailed further in Table 3.3.

Table 3.3 Main wastewater sources with their collection sumps

Sump	Wastewater Sources
No. 1 (BF)	Gas scrubbing, slag quenching and water from blast furnaces
No. 2	Collection sump before discharge via long sea outfall
No. 3	Water from Arnallt Stream, storm water and emergency overflows
No. 5 (BOS)	Gas scrubbing water from BOS plant
No. 6 (Morfa)	Morfa Coke Ovens wastewater
No. 10	Stormwater from the old Grange coke area and stockpiles
Con Cast	Wastewater from continuous casting area
Cold Mill	Treated pickle liquor, rinse water, and rolling emulsion from Cold Mill
Deep Drain	Abbey treatment plant, overflows (Hot Mill), road drainage and filter backwashes
CAPL	Wastewater from the Continuous Annealing Plant

Deep Drain is by far the largest wastewater collector and acts as a central reservoir for a number of sources of effluent from several processes including cooling water overflows, filter backwashes, de-mineralisation plant effluent and basement drainage. Deep Drain also acts as a collection point for most of the road drainage, a collection point for sump overflows and filter backwashes. The pipe networks leading to the deep drain covers a vast area including the Cold Mill.

In order to remove oil from the effluent, oil skimmers are used in most of the sumps prior to pumping the water to the Nautilus or Sump No. 2 and to Long Sea Outfall.

The Energy Operations Department oversees the overall effluent network, its operations and maintenance, while since 2011 Nalco has been in charge of the Steelworks effluent treatment operations. Until 2011, Nalco was in charge of the Steelworks heavy-end facilities water treatment and GE Water & Process Technologies take care of the light-end facilities water treatment as well as run the Nautilus final effluent treatment plant.

3.3.1 Effluent Water Flows

The total volume of effluent water discharged from the Port Talbot Steelworks is approximately 1500 m³/h or ~13 million m³/annum (2008). In order to understand the effluent flow volumes, meters have been previously installed to pipes entering or leaving the sumps. This data was used to get an understanding of the effluent flows within the Works and based on this, Figure 3.6 shows the division of approximate volumes for wastewater flows into different sumps in 2008.

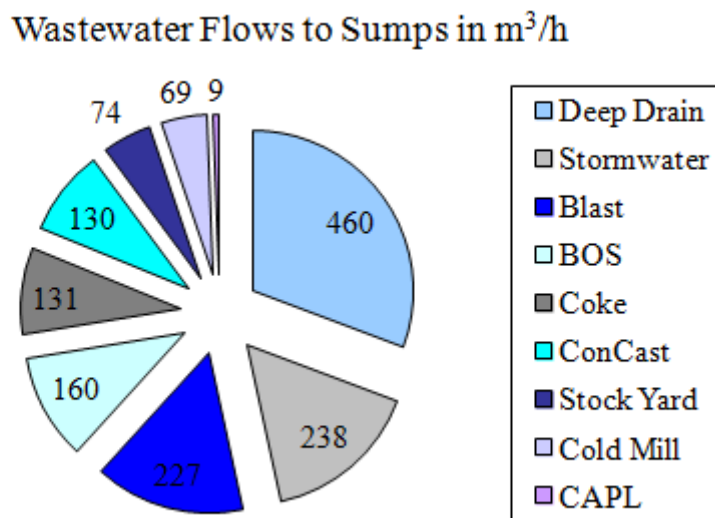


Figure 3.6 Wastewater flows into sump No. 2 (m³/h) in 2008

2008 was the first year when the sump flows were metered comprehensively and although the production capacity was dropped in the last quarter of the year, the meter readings give a good general idea of the wastewater flows to specific sumps.

As demonstrated in Figure 3.6, the Deep Drain is receiving by far the greatest amount of effluent, at 460 m³/h, which equals to approximately 30% of all the effluent produced,

the second biggest share consists of Sump No 3 and BOS stormwater with an approximate 15% share. The biggest individual wastewater producing facility is the Blast Furnaces, which produce on average 227 m³ of effluent water per hour, which is a 15% share of the total effluent production flows. Other big effluent producers include the BOS Plant with a 11% share, Coke-Ovens and Continuous Casting Plants with a 9 % share each. Coal Stock Yard and Cold Mill are some of the smaller effluent producers, both with a 5% share, while CAPL is the smallest effluent producer with its mere 9 m³/h or 1% of the total annual effluent production. What should be noted is that the Dock water return is not included in this Figure.

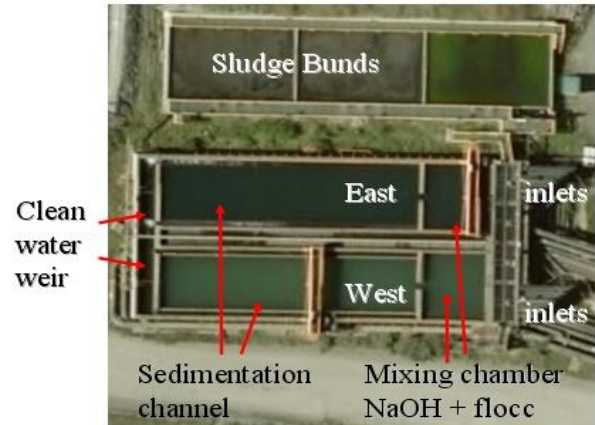
3.3.2 Nautilus Final Effluent Water Treatment System

After being treated at the site-specific wastewater treatment plants, all the final effluent arising within the site is either collected to Sump No. 2 or is pumped to Nautilus for further treatment. Nautilus is a set of sedimentation channels, built by Quasar Chemicals Ltd, which were taken into use in 1999 to reduce suspended solids, especially zinc and oil, in the effluent discharged from the Port Talbot Steelworks prior to it entering the sea via the Long Sea Outfall.

There are several possible effluent input streams to the Nautilus water treatment system, including: Cold Mill Effluent Plant, BOS Plant (RHK TB Degasser), Deep Drain, Clarification Plant effluent from MPH as well as Sumps No. 1 (Margam Blast Furnace Effluent), No. 3, No. 5 (BOS Plant effluent), No. 6 (Morfa Coke- Ovens effluent) and No. 10 (stormwater). Since a series of breaches in zinc consent limits at the Long Sea Outfall discharge point in 2005, the most zinc-containing effluents have consistently been run through the Nautilus sedimentation channels. Some of the most zinc-containing effluent streams include Sump No. 5 (BOS Plant effluent), which contains high concentrations of insoluble zinc and Sump No. 1 (Blast Furnace effluent), which contains high insoluble concentrations of zinc and lead. At any given time, there are 3-4 different flows to both channels and these can be manually altered. As an example, when in full working order, due to the high amount of solids present in the flows, Nautilus could include to East channel: CAPL, Sump No. 3 and No. 1 and West channel: Sump No. 5, No. 6 and 10.

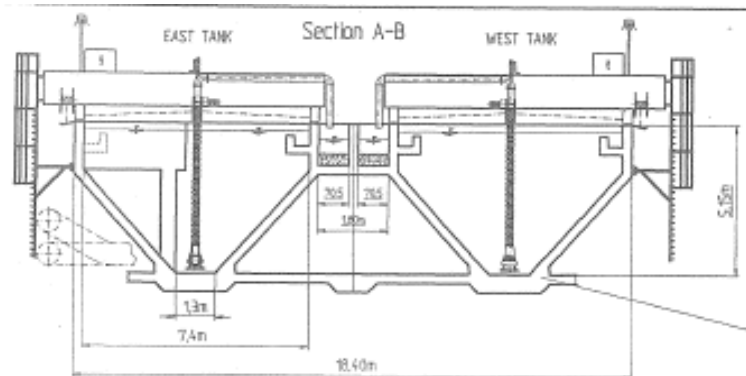
As the wastewater enters the Nautilus treatment system, the metals are in a stable, dissolved aqueous form and therefore are unable to form solids. In order to enable flocculant settling, the effluent entering the Nautilus is mixed with sodium hydroxide (NaOH) and flocculant in a mixing chamber (Figure 3.7).

Figure 3.7 Picture of the Nautilus water treatment system from the top (Google Maps Website)



The goal of the rapid mixing operation is to first raise the pH of the wastewater to form metal hydroxide particles, followed by enhancing the polymer attachment to the metal solid particles. As a consequence, the small metal hydroxide particles become entangled in these polymers, causing the particle size to increase (form flocs), which promotes the settling process. Once the particles become enmeshed in the polymer, they become heavier than water and settle to the bottom of the Nautilus sedimentation channels.

Figure 3.8 Horizontal cross-section of the Nautilus sedimentation channels (Drawing Office, 2007)



Nautilus consists of two, 43.2 metres long, 7.4 metres wide and 5.15 metres deep sedimentation channels, where dissolved solids are dropped out of solution and solids, especially suspended solids sedimentate to the bottom with the help of alkali and flocculant. The bottom of the Nautilus is V-shaped (Figure 3.8), so that the residue

sludge settling to the bottom is then sucked away with a hose that moves up and down the sedimentation channels with a help of a ‘bridge’ (crane) as can be seen in Figure 3.9.

Figure 3.9 Picture of one of the Nautilus sedimentation channels and the crane



During the Nautilus water treatment system operations, the clean water overflows to a clean water corridor, next to the sedimentation channels, from where it travels to a weir at the end of the sedimentation channels. From the weir, the clean water is gravity fed to the Steelworks final effluent receiving Sump No. 2. The sludge settling to the bottom of Nautilus is sucked to a sludge channel located in the middle of the two sedimentation channels. From the sludge channel the sludge is gravity fed to 4 m x 4 m sludge bunds (Figure 3.7) that are located next to the Nautilus plant. The purpose of the bunds is to drain out (dewater) the sludge.

Prior to introducing the filter press in the Steelworks site in autumn of 2007, there were issues with landfilling the sludge generated in Nautilus as the oil and moisture content were too high for the sludge to be landfilled under the Landfill Directive (2005). There was no facility to store the sludge on the site either, so Nautilus was taken out of use in 01/10/2006 until 07/08/2007. There is also a recurring problem with large solids of Mill and ConCast scale building up to the bottom of the settling tanks and blocking the chambers. Manual sludge removal by the Energy Department is then required to remove the sludge build up.

3.4 Steelworks Wastewater Constituents

Due to the nature of steelwork activities, several impurities are present in discharge waters. The National Center for Manufacturing Sciences (2004) conclude that wastewater emissions from coke oven plants, blast furnaces and BOS furnaces are the

most relevant emissions to water from steelworks. According to Yoon-Gih Ahn (2006) the key constituents from a steel-making facilities are listed in Table 3.4

Table 3.4 Unwanted constituents arisen during steelworks operations

Facility	Constitituents
Coke Ovens	Phenol, cyanide, ammonia, oil and grease, suspended solids
Sintering Plant	Suspended solids
Steel Melting	Suspended solids
Blast Furnace	Suspended solids, cyanide
Rolling Mill	Oil and grease, acids

As can be seen in Table 3.4, coke oven effluents have the most complex constituents, including phenol, cyanide, ammonia, oil and grease and suspended solids. Overall suspended solids, which include mostly different metals, is the most commonly found constituent in the steelworks effluent.

3.4.1 Discharge Consent Limits

There are altogether 5 different points for discharge at the Port Talbot Works. These, with their receiving waters, are listed in Table 3.5.

Table 3.5 Port Talbot Steelworks discharge points (Environment Agency, 2004)

Name	Discharge Point
Long Sea Outfall	Swansea Bay
Site run off and treated site effluent	Arnallt Culvert
River Arnallt and floodwater surface drainage	Swansea Bay
Iron ore stockyard	Afan Estuary
Cooling water discharge	Port Talbot Dock

Out of the 5 discharge points, Long Sea Outfall (LSO) plays the most important role as seen in Figure 3.3 before and is the only one governed by the Environment Agency as explained next.

Port Talbot Works is subject to consent limits for discharges to the aqueous environment. These are set within the Integrated Pollution Prevention and Control (IPPC) Permit by the Environment Agency. These consent limits have traditionally been either in terms of concentration (e.g. mg/L) or daily mass limits, but in the most

recent permit there are now limits for both. The Environment Agency sets these consent limits for Long Sea Outfall as seen in Table 3.6 below.

Table 3.6 Long Sea Outfall effluent discharge consent limits from 2006 onwards

DETERMINANTS	LONG SEA W1	
pH	6 - 10	
Suspended Solids (kg/day)	27500	
Suspended Solids (kg/annum)	2250000	
S.Solids (mg/l) - monthly average	150	
Flow (m ³ /day)	70000	
Flow (m ³ /hour)	6000	
Temperature (°C) - daily average	40	
Temperature (°C) - hourly average	45	
Oil (kg/day)	3150	
Oil (kg/annum)	360000	
Oil (mg/l) - monthly average	25	
Cyanide (kg/day)	45	
Cyanide (kg/annum)	2700	
Cyanide (mg/l) - monthly average	0.2	
Ammonia (kg/day)	4000	
Ammonia (kg/annum)	400000	
Ammonia (mg/l) - monthly average	27.5	
Phenol (kg/day)	350	
Phenol (kg/annum)	18000	
Phenol (mg/l) - monthly average	2	
Soluble Zn (kg/month)	2100	
Soluble Zn (kg/annum)	N/A	
Soluble Zn (mg/l) - monthly ave.	2.5	
Soluble Pb (kg/month)	300	
Soluble Pb (kg/annum)	N/A	
Soluble Pb (mg/l) - monthly ave.	0.3	
Soluble Cr (kg/month)	200	
Soluble Cr (kg/annum)	N/A	
Soluble Cr (mg/l) - monthly ave.	0.2	
PAH's (kg/month)	250	
PAH's (kg/annum)	N/A	
PAH (mg/l) - monthly	1	

3.4.2 Wastewater Constituents against Consent Limits at the Long Sea Outfall

Daily water samples and meter readings are taken from the Long Sea Outfall prior to discharge in order to get an understanding on how LSO effluent compares against the consent limits and to prevent a breach of consent limits. The information gathered from the LSO or the individual sumps has never, however, been analysed. The graphs that now follow show the daily discharge values in relation to the current consent limit.

Firstly, when looking at the averaged values for daily flows from LSO per month in 2007 against the limit value of 70,000 m³, it can be seen that the discharges are well within consent (Figure 3.10). In fact, the highest flow value for the year is only 65,120 m³ on 14th May 2007.

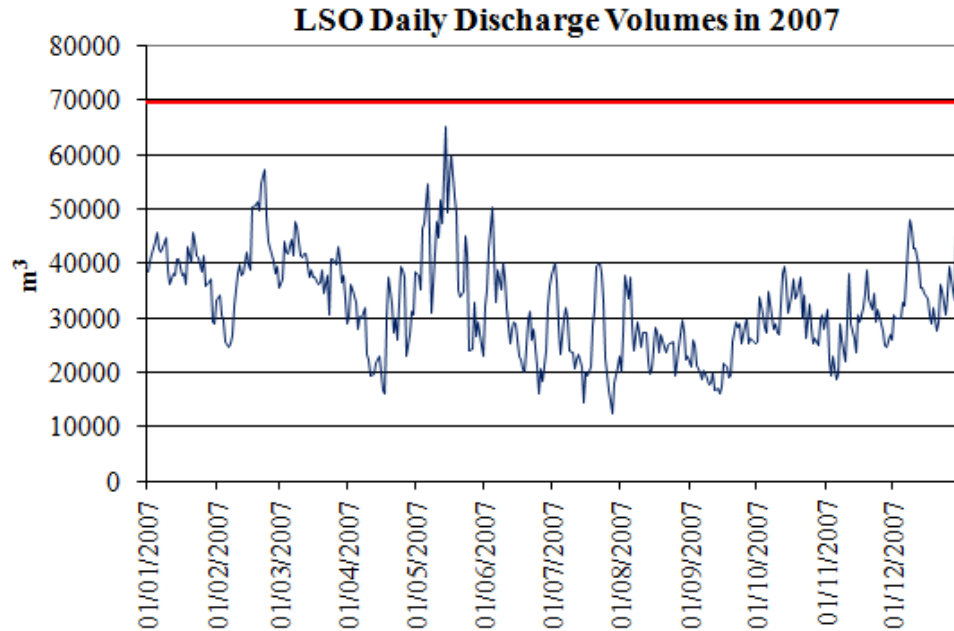


Figure 3.10 LSO daily average flows in 2007

Similarly the daily discharge values for pH fall easily between the consent limit of 6-10 as can be seen in Figure 3.11. In fact, the individual LSO daily pH values did not breach the consent limit once during 2007.

One of the major constituents present in Steelworks' effluent water is suspended solids i.e. un-dissolved matter, which often includes inorganics such as metals. As can be seen in Table 3.6, Port Talbot's daily consent limit for suspended solids is 150 mg/L and as can be seen in Figure 3.12, the daily values for suspended solids in LSO are often around the mark of 50 ppm. Despite the good average values of suspended solids, the daily consent limit (Table 3.6) of suspended solids was breached 3 times during 2007. Once in January the value was 168 mg/L, in June values of 188 mg/L and 165 mg/L were recorded, as can be seen in Figure 3.12.

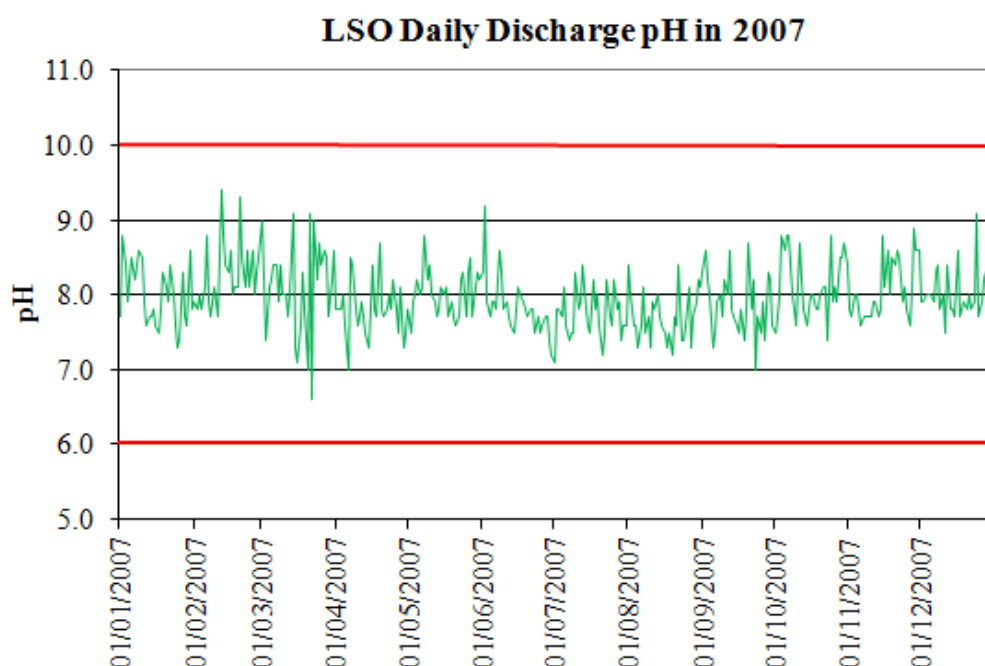


Figure 3.11 LSO daily average pH in 2007

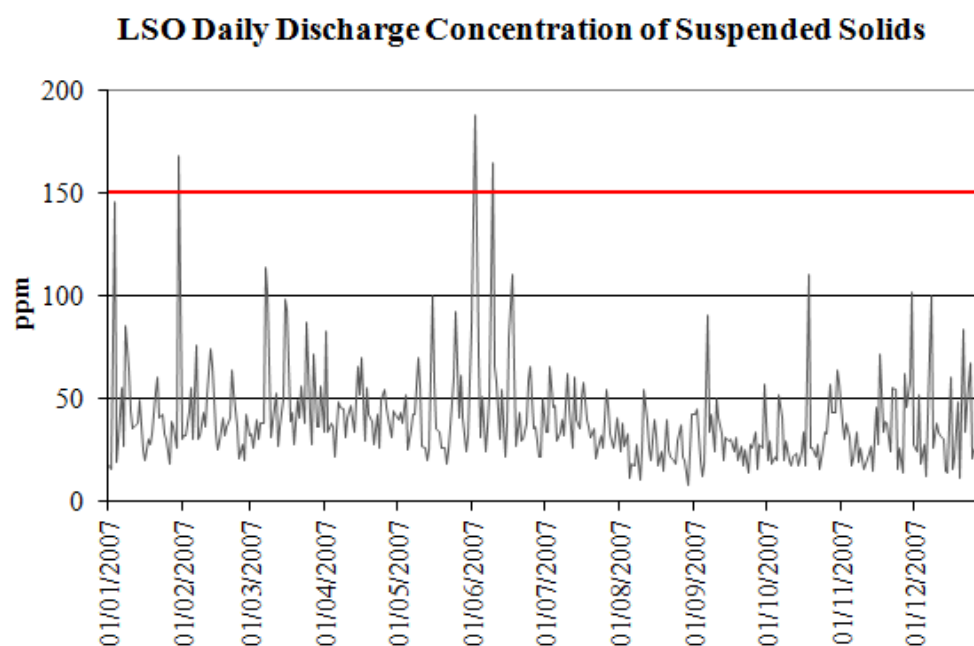


Figure 3.12 LSO Daily average suspended solids concentration in 2007

In recent years there have been several breaches of zinc concentration in the Port Talbot Steelworks discharges and therefore there's a special interest in the zinc levels of the LSO discharge. As can be seen in Figure 3.13, in 2007 there are a few breaches in the daily soluble zinc concentration.

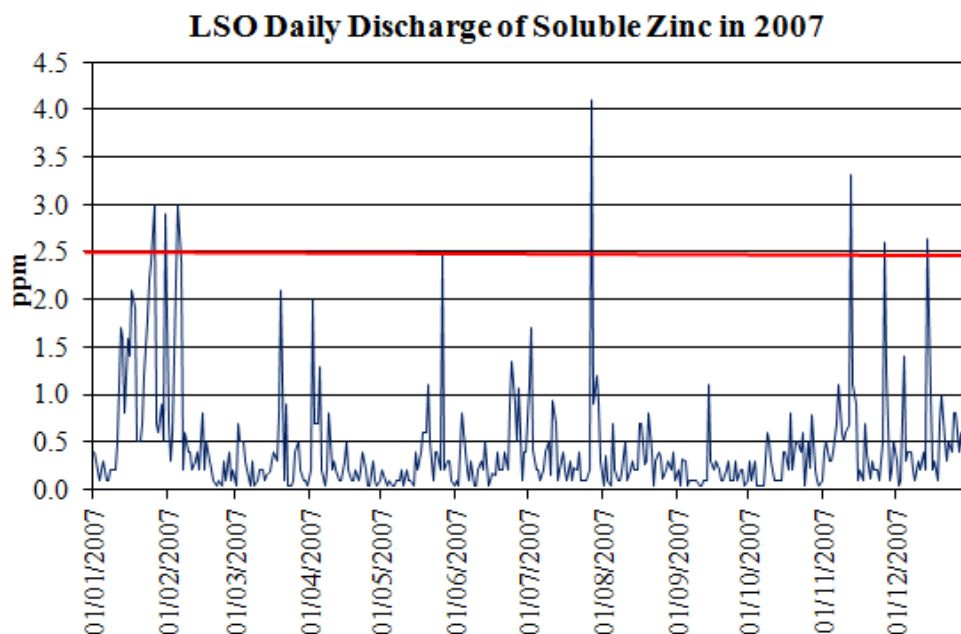


Figure 3.13 LSO daily average soluble zinc concentration in 2007

The concentrations of soluble lead and chromium on the other hand are well within consent limits in the LSO discharge water. Another constituent with occasional breaches is oil as seen in Figure 3.14.

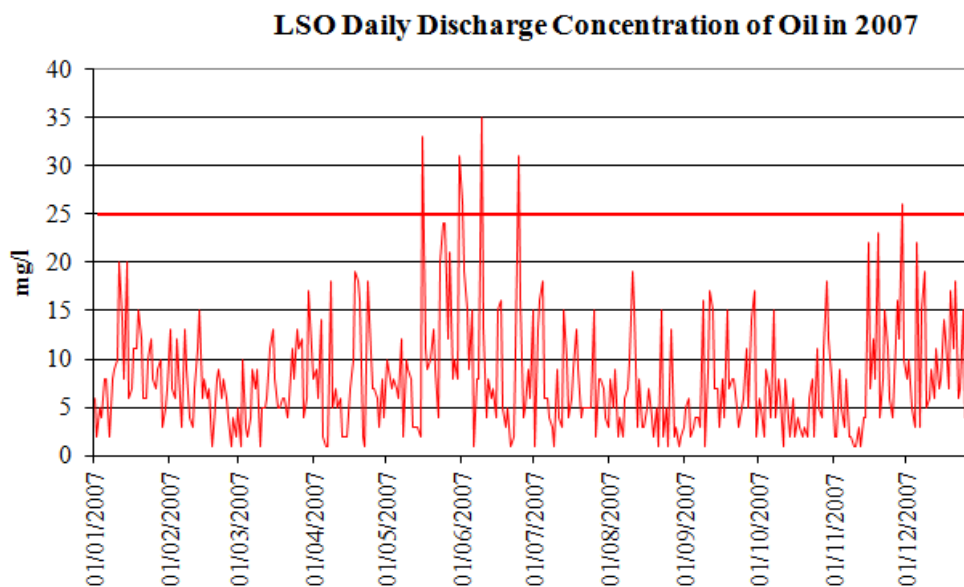


Figure 3.14 LSO Daily average oil concentration in 2007

3.4.3 Wastewater Constituents against Consent Limits at the Facilities

Even more interesting than looking at the individual concentrations in the Long Sea Outfall, is to try to understand where the specific pollutants have entered the final effluent. The following graphs present constituents in individual sumps within the Port Talbot Steelworks. The Blast Furnace and the BOS Plant have been found to be the main sources of the insoluble metals, whereas the Cold Mill (CM) was found to be the major source for soluble metals (Swindley et al., 1998), where as Rees (1996) identified the Cold Mill and Deep Drain as the areas where the wastewater streams are more likely to contain oil.

The sump with the largest range of constituents and often one of the highest constituent concentrations is Sump No. 6, which is the Morfa Coke-Ovens sump. The zinc and suspended solids concentration that are on occasion breached at the Long Sea Outfall are however generated during the operations of the other facilities and the Steelworks overall operations as will be explained now.

The sumps with the highest concentrations of suspended solids in their effluent water include Cold Mill (Figure 3.15), CAPL (Figure 3.16), BOS Plant (Figure 3.17) and Continuous Casters Sump (Figure 3.18). Out of these, the Cold Mill and CAPL have by far the most consistently high concentrations.

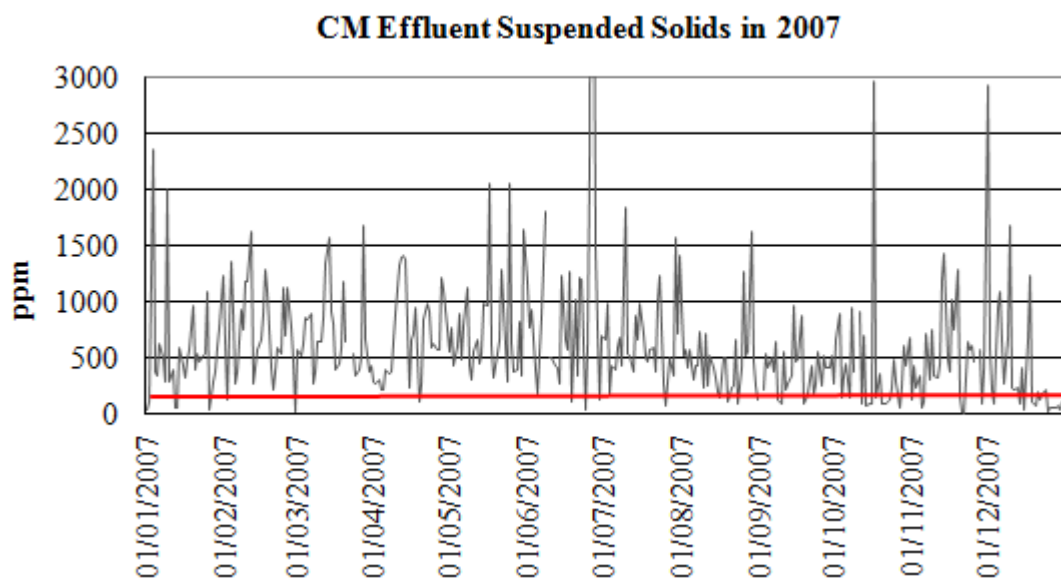


Figure 3.15 Cold Mill effluent sump daily suspended solids Concentrations in 2007

When looking at Figure 3.15, it is clear that the CM effluent suspended solids concentration is rarely lower than the 150 ppm consent limit. Based on calculations using daily values, the average concentration of suspended solids at this Sump in 2007 was in fact 1008 ppm.

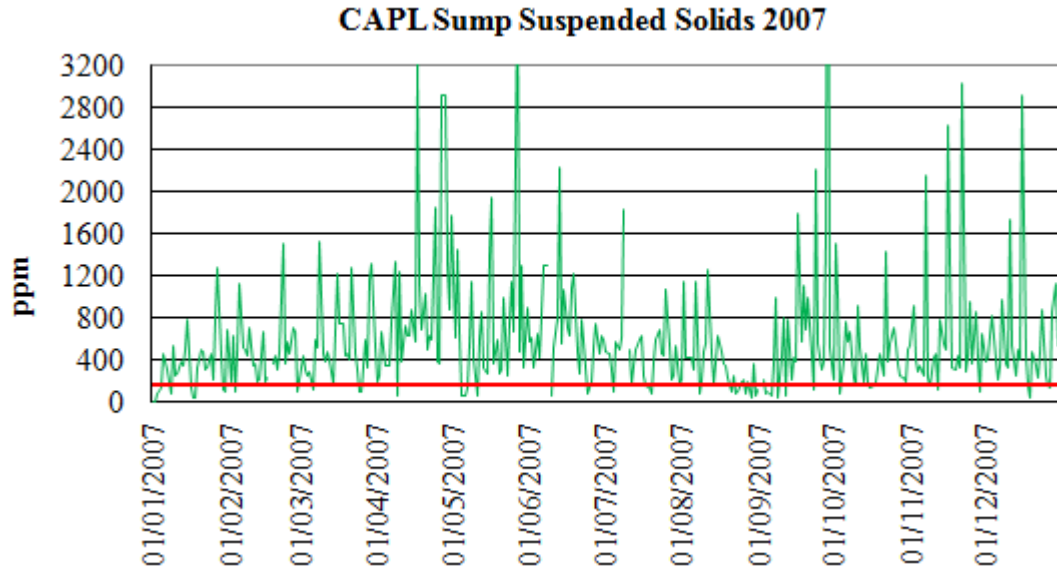


Figure 3.16 CAPL effluent sump daily suspended solids concentrations in 2007

Despite the high concentrations of suspended solids at the Cold Mill (Figure 3.15) and CAPL (Figure 3.16) operations, the volumes of these effluents are low in relation to the total flows (Figure 3.6) and by the time these effluents arrive to the Long Sea Outfall final discharge point, the suspended solids concentrations have been diluted down by some of the streams with higher volumes, but lower suspended solids concentrations.

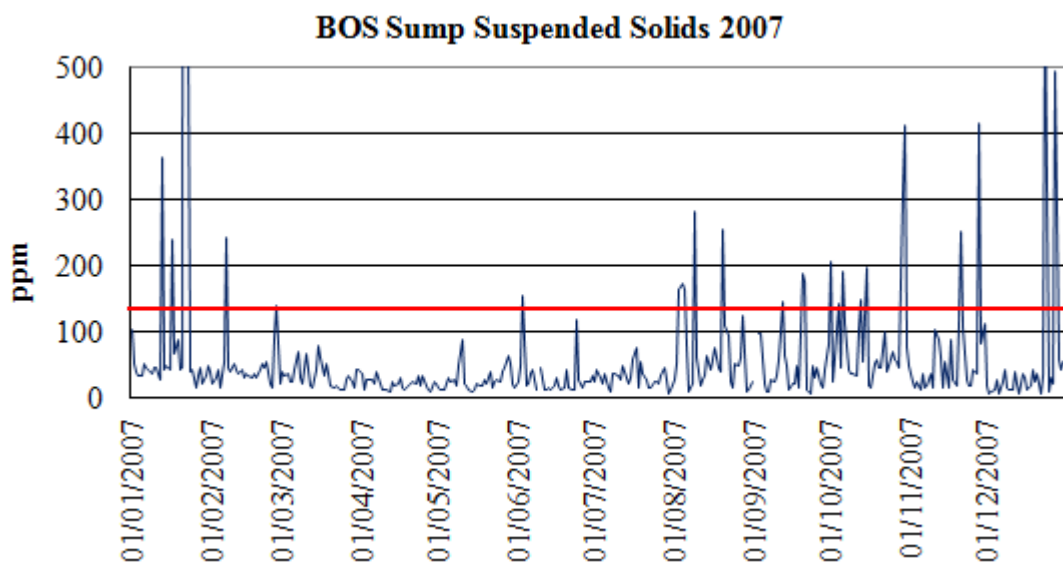


Figure 3.17 BOS Plant effluent sump daily suspended Solids Concentrations in 2007

Though, to a lesser extent, the BOS (Figure 3.17) and ConCast (Figure 3.18) effluents also contain high concentrations of suspended solids of an average 174 ppm and 134 ppm respectively. More importantly, these two facilities generate effluent at higher volumes and therefore also contribute significantly to the total concentrations of suspended solids at the Long Sea Outfall.

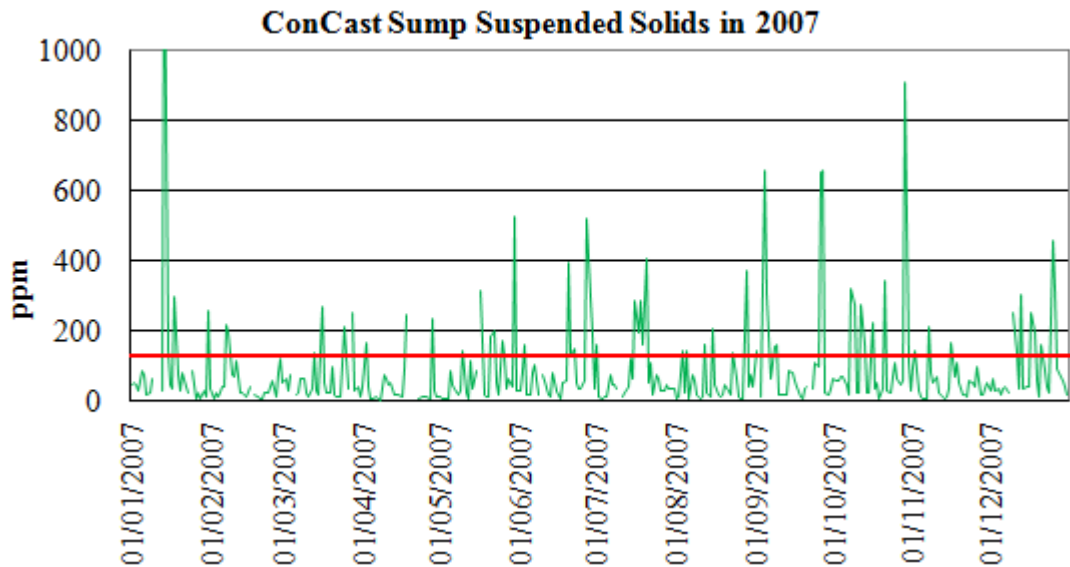


Figure 3.18 ConCast effluent sump daily suspended solids concentrations in 2007

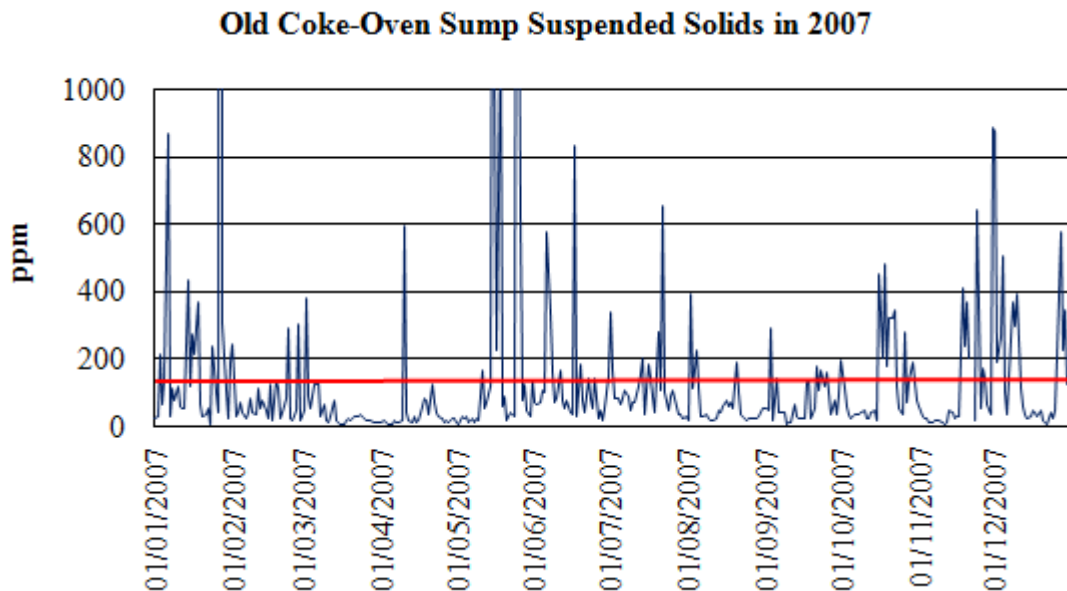


Figure 3.19 Sump No 10 effluent sump daily suspended solids concentrations in 2007

The old Grange Coke-Ovens effluent water receiving sump number 10 currently receives most of the road drainage from the Works. As can be seen in Figure 3.19, in

relation to the 150 ppm consent limit of the LSO, the road drainage water has, on occasion, a very high concentration of suspended solids. This is expected to happen during heavy rainfall, when the rain water flushes the dust from the roads and transports it to Sump number 10.

Sumps with lesser concentrations of suspended solids include the Blast Furnaces Sump No. 1 as can be seen in Figure 3.20 below.

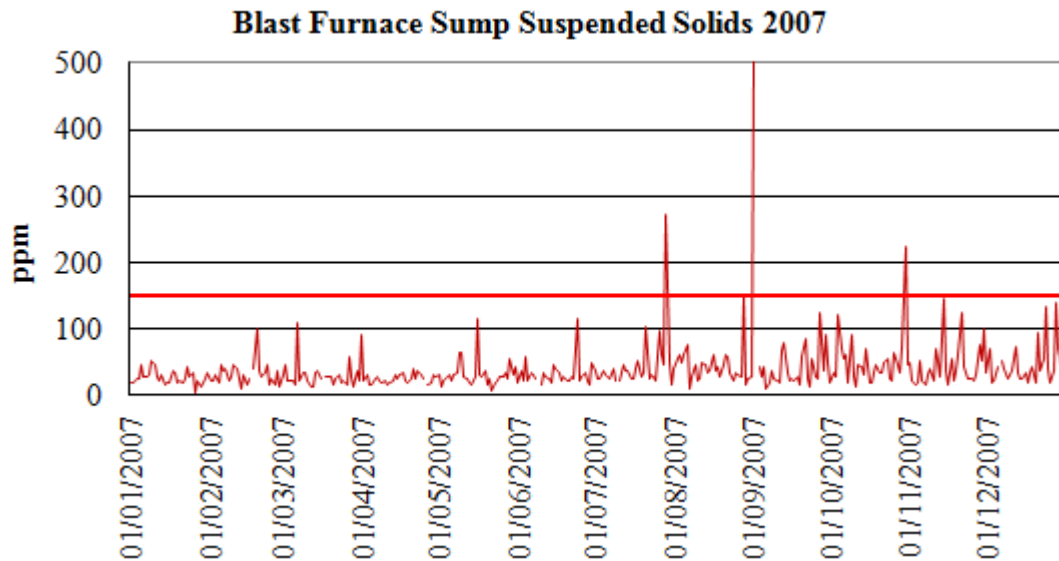


Figure 3.20 Blast Furnaces effluent sump daily suspended solids concentrations in 2007

Looking specifically at the concentrations of suspended solids within the effluent sumps of the individual facilities, it becomes evident that overall higher concentrations of suspended solids than the 150 ppm consent limit at the LSO are generally found. However, the average concentrations of the suspended solids at the LSO throughout the year 2007 were 40 ppm. The low concentration can be explained by the efficiency of the Nautilus final effluent treatment plant and perhaps low concentrations of suspended solids at the Deep Drain, which has high flows, but from where, unfortunately, no data is available.

Despite not having an especially high amount of suspended solids present in its effluent water, Blast Furnace effluent Sump No. 1 is the one with by far the highest soluble zinc concentrations highlighted in Figure 3.21. Taken that the Blast Furnace also generates large volumes of effluent (Figure 3.6) in relation to most of the other facilities, it is the

main source of soluble zinc in the effluent within the Steelworks. The average soluble zinc concentrations at Blast Furnace Sump no 1 throughout the year 2007 was 4 ppm.

As seen in Figure 3.21, there are a few clear soluble zinc spikes present at the Blast Furnace effluent soluble zinc concentrations. When comparing these spikes to the concentrations of soluble zinc at the LSO (Figure 3.13) it becomes clear that there is a direct link between the high concentrations of zinc at the Blast Furnace effluent and the effluent at the Long Sea Outfall. In order to find out what causes the high concentrations, more research into the Blast Furnace operations and effluent generation is required.

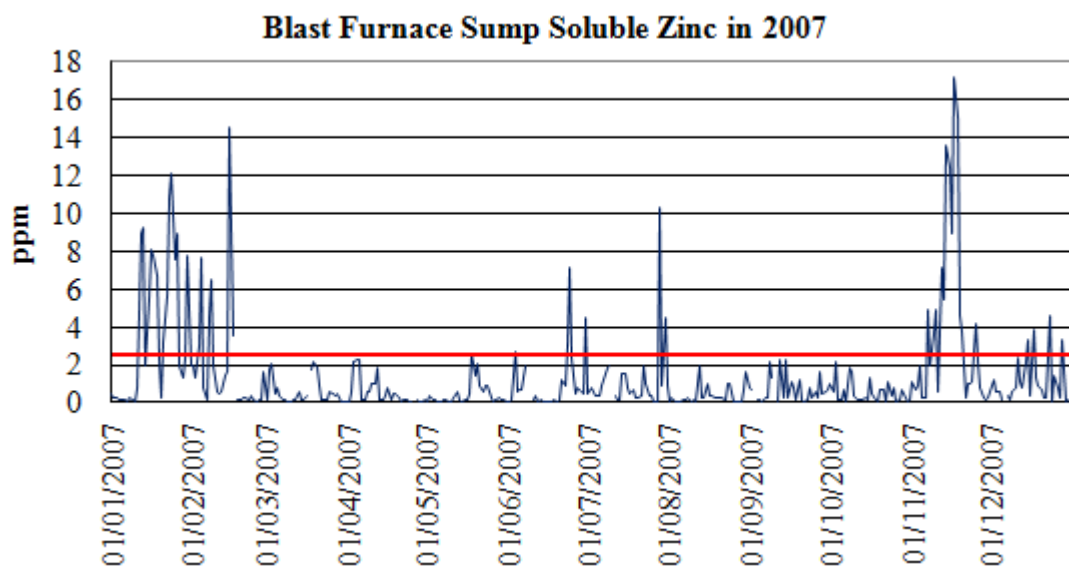


Figure 3.21 Blast Furnaces effluent sump daily soluble zinc concentrations in 2007

Another sump with high soluble zinc concentrations is the Continuous Casters Sump (Figure 3.22). The BOS Plant effluent Sump No. 5 (Figure 3.23) has also heightened, albeit lower than Blast Furnace and Continuous Casters, effluent soluble zinc concentrations. The concentration present at the above sumps in relation to LSO consent limits follows.

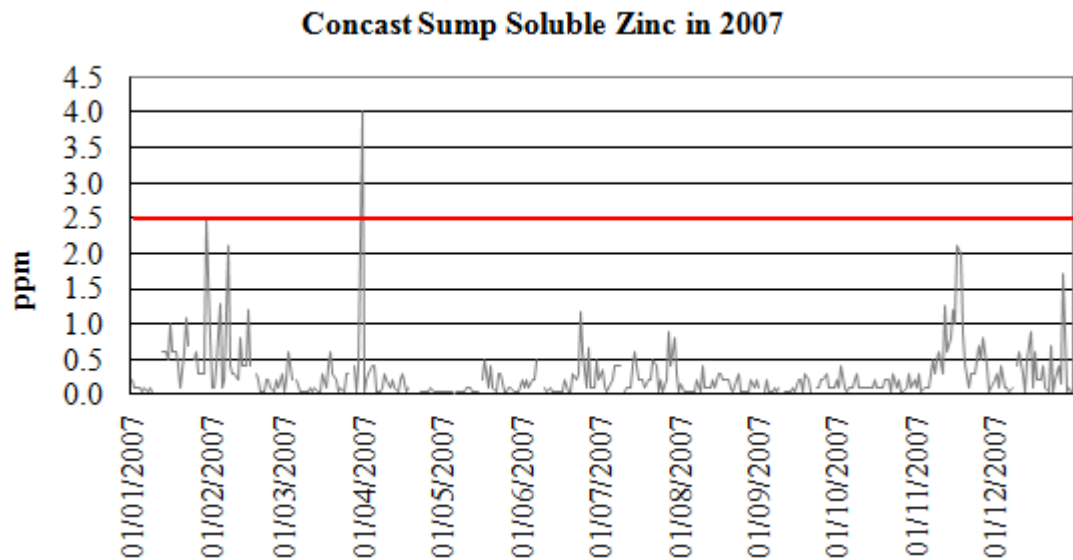


Figure 3.22 ConCast Plant effluent sump daily soluble zinc concentrations in 2007

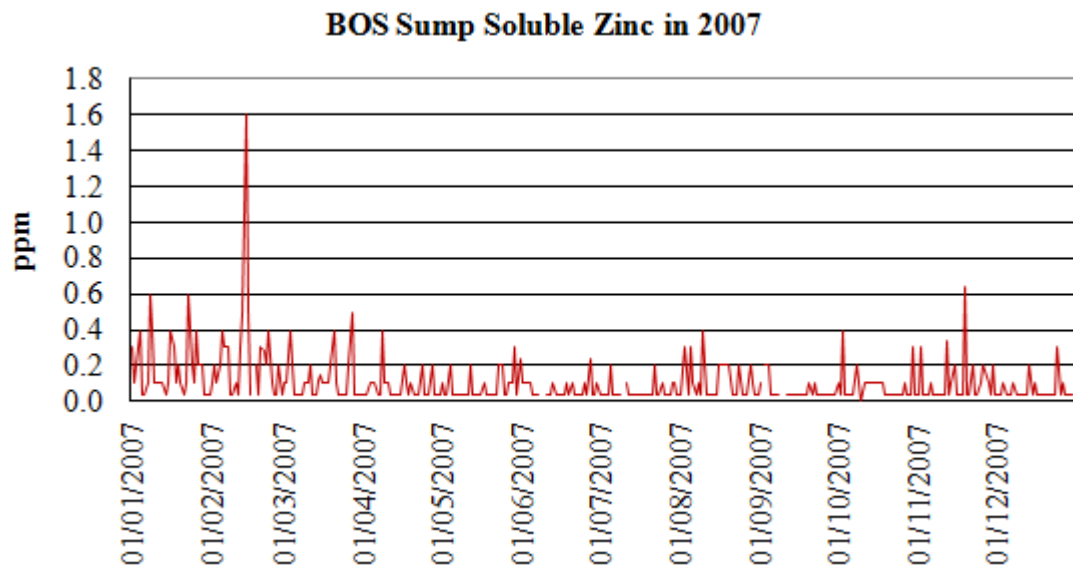


Figure 3.23 BOS Plant effluent sump daily soluble zinc Concentrations in 2007

3.4.4 Nautilus Final Effluent Treatment System Performance Results

Nautilus influent and effluent waste water streams have been analysed in order to get an understanding on how this final effluent treatment system performs in removing suspended solids from the waste water. When the Nautilus treatment system is in use it is performing well as can be seen in Figure 3.24. The red bar outlines the combined concentration of suspended solids in influent entering the West and East channels,

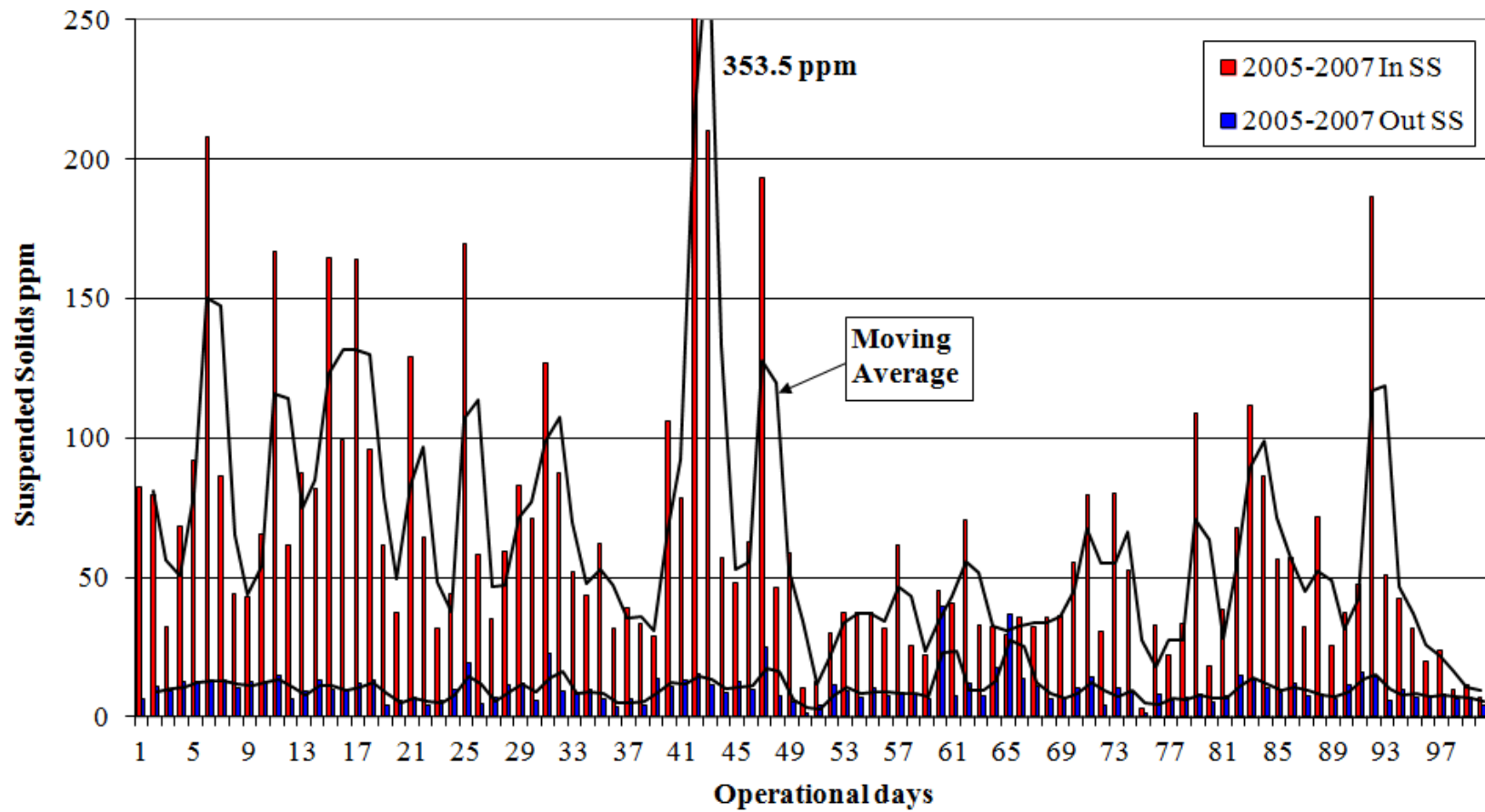
Nautilus SS Weekly Average Influent v. Effluent in 2005-2007

Figure 3.24 Nautilus water treatment system weekly combined influent versus effluent in 2005-2007

where as the blue bars outline the combined concentration of suspended solids leaving the treatment system in effluent. Daily water samples of water are taken from the inlet pipes to Nautilus and the clean water wier, but until here no analysis of this data has been carried out.

In order to look at the removal efficiency of the Nautilus treatment system during the years 2005 to 2008, the total concentration of suspended solids entering the treatment system within were compared against the total concentrations leaving the system within the same year. As can be seen in Figure 3.25, in 2005, the treatment system removed 38055 ppm of suspended solids out of the 43033 ppm entering the system. Thus, leaving an effluent concentration of 4978 ppm, equalling to a removal efficiency of 88%. From 2006-2008, the removal efficiencies were 74%, 81% and 75% respectively.

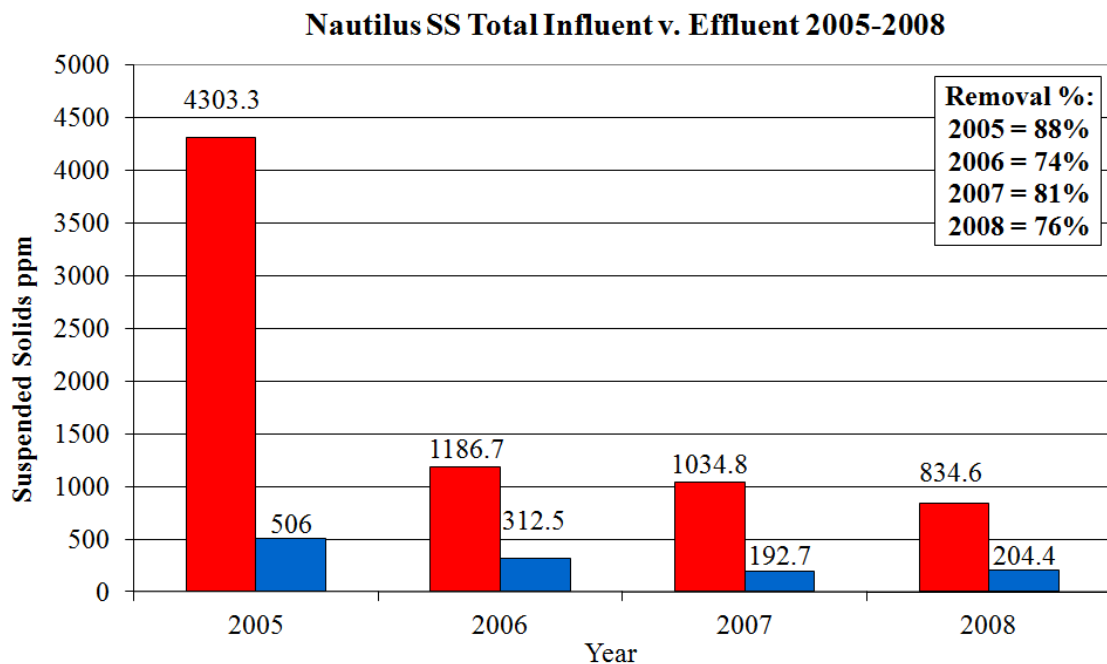


Figure 3.25 Nautilus water treatment system performance in 2005-2008

Unfortunately, there have been consistency issues with the Nautilus water treatment system. In fact, during 2005-2007, the treatment system was in operation only for some 100 days, as can be seen in Figure 3.24.

The disruptions in using the treatment system were due to having issues with storing the generated sludge and the sludge pumps not working, in both cases leading to solids accumulating to the bottom of the Nautilus sedimentation channels. Until the end of

summer 2007 there was no effective system to remove solids from the bottom of the sedimentation channel and therefore the treatment system was out of use between 16/09/2006 and 07/08/2007. In autumn 2007 a filter press was taken into use in order to dewater and remove the oil from the sludge faster and more effectively, so the sludge could be landfilled. After July 2009 no landfilling of sludge was allowed due to the implementation of the new Landfill Directive.

3.4.5 Nautilus Effluent Treatment System Performance Experiment

In order to get a better understanding on what was happening in the Nautilus effluent treatment system, the author instigated an experiment looking into the specific treatment efficiency of the Nautilus East and West Channels. During the experiment, GE was taking daily effluent treatment samples from the mixing chamber, where all the incoming effluent is mixed together and from the clean water weir. These samples were then transported by the GE to the Chemical Laboratories of the Port Talbot Steelworks, who carried out the analysis. Due to the alkali present at the mixing chamber, the pH of the samples was first dropped to 1 using hydrochloric acid (HCl) prior to carrying out the analysis using Inductively Coupled Plasma mass spectrometry (ICP-MS).

It has been estimated by the Energy Department that when in operation, 1/3 of all the Port Talbot Steelworks final effluent is treated at the Nautilus water treatment system. More than 60% of this volume is treated at the West Channel. However, the streams with more and higher concentrations of unwanted constituents, especially zinc are treated at the East Channel.

The most important results of the Nautilus effluent treatment experiments will now be outlined.

3.4.6 Nautilus Effluent Treatment System Performance Experiment Results

Both the West and East Sedimentation Channels have fairly consistent and efficient solids removing capacity, as can be seen in Figure 3.26 and 3.27, although it is evident that there are effluent streams with higher suspended solids and zinc concentrations

treated via the East Channel than the West Channel. The solid and zinc concentration peaks at the East Channel are overall higher and there are several more peaks at over 1000 ppm in the East Channel flows.

When comparing the Nautilus treatment efficiency against the Long Sea Outfall 150 ppm suspended solids consent limit (Figure 3.26), it appears that both the Nautilus East and West Sedimentation Channels are able to achieve a removal efficiency of suspended solids that is better than the consent, no matter how high the initial influent suspended solids concentrations.

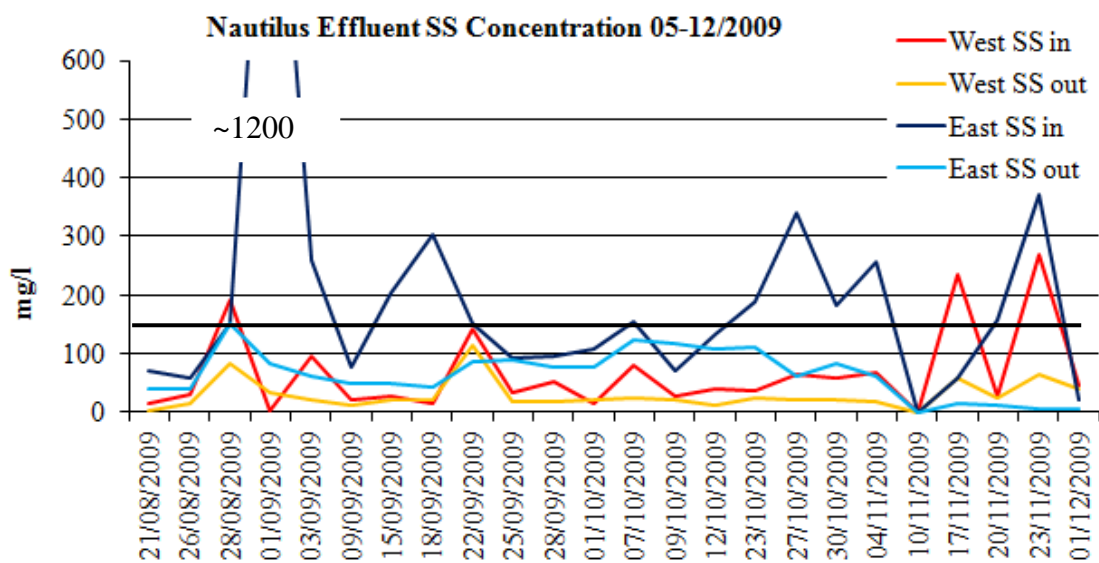


Figure 3.26 Nautilus East and West Channel removal efficiency of suspended solids

When analysing the treatment efficiency of the Nautilus final effluent treatment system against the soluble zinc 2.5 ppm consent limit (Figure 3.27), it can be seen that on occasion the zinc concentrations at the effluent leaving the Nautilus West Sedimentation Channel treatment system are higher than the consent limit at the LSO outfall.

When comparing the peaks within Figures 3.26 and 3.27, it appears that the high concentrations of the suspended solids and zinc occur simultaneously. The peaks detected have been investigated and they have been linked to clarifier cleaning activities within the site. During the cleaning, the sludge generated at the bottom of the clarifier is

dredged which results in the mixing of the clean water and the sludge and results in a peak at the effluent treatment.

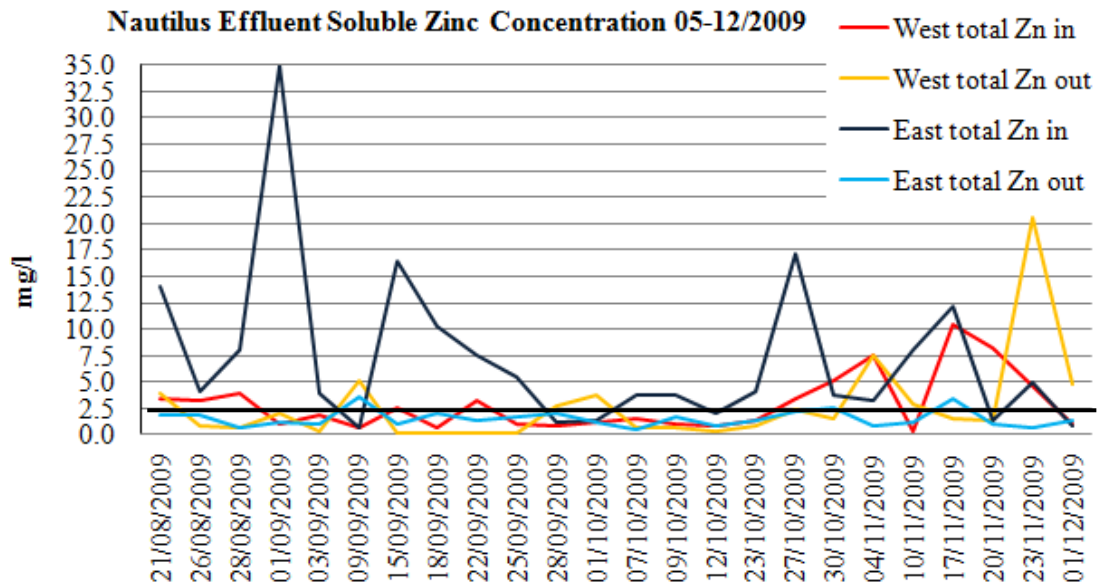


Figure 3.27 Nautilus East and West Channel removal efficiency of zinc

3.5 Facility-Specific Water Systems

Next to the Energy Operations Department overseeing supply and effluent water systems described above, each of the eight Port Talbot Steelworks facilities have their own individual water and wastewater systems. A full water mass balance for all the major facilities and processes within Port Talbot Steelworks can be seen in Figure 3.28.

The full water mass balance was initially developed by the Energy Operations Department in 2005. Following the work carried out for Figure 3.3 and in order to attain information required for the water benchmarking survey outlined in Chapter 4, the author updated the full water mass balance with water flow information for 2007. The Figure 3.28 outlines all the major water sources and water treatment plants in their own colour giving a better picture on what the biggest water sources are and where a specific type of water is being used within the Works. Water consumption and effluent generation in different facilities will be explained in more detail later in this chapter.

Updated for 2007

Port Talbot Works Typical Water Balance

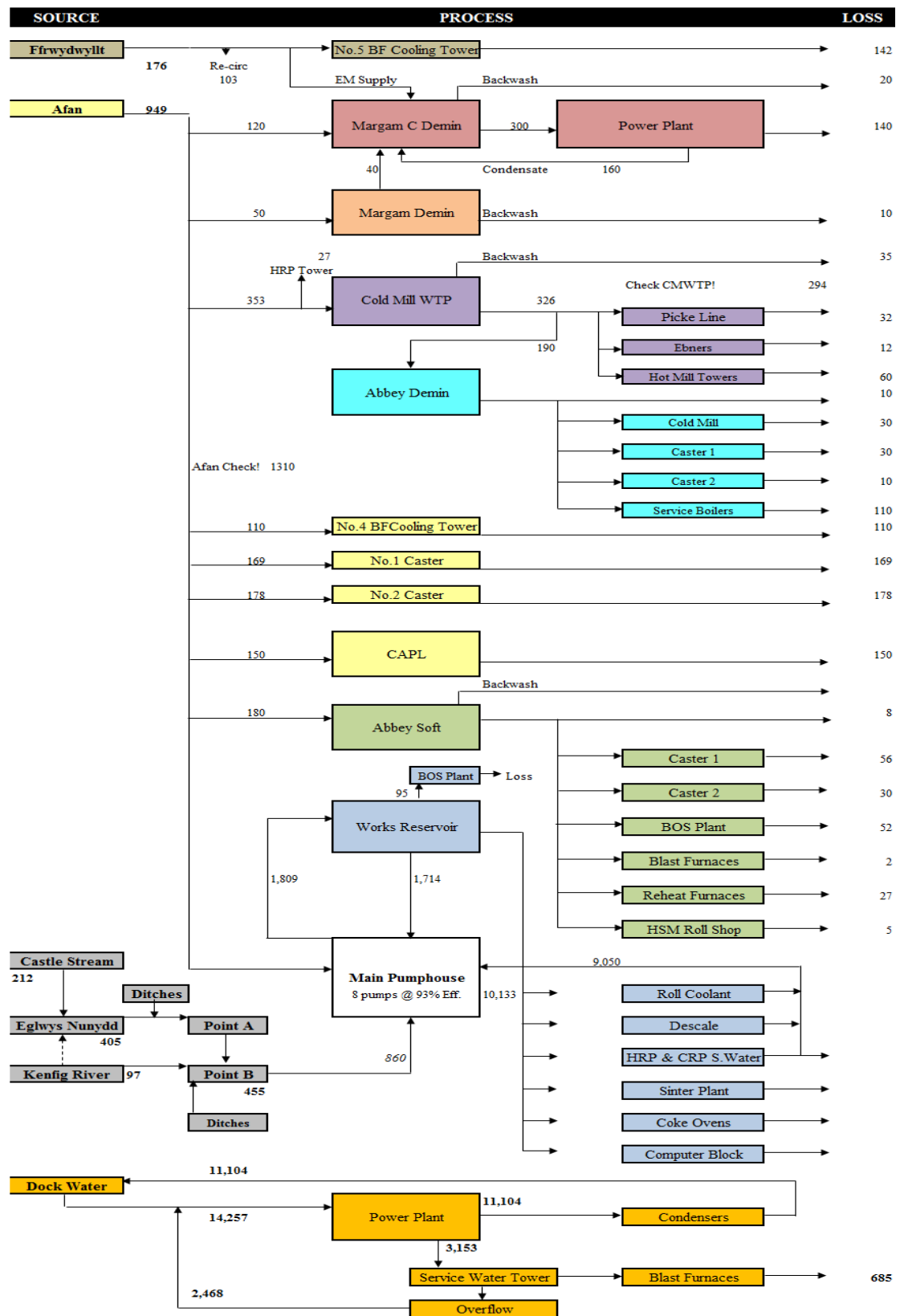
UNITS: averages m³/hr

Figure 3.28 Port Talbot Steelworks full water mass balance (adapted from Energy Department, 2005)

The work carried out in order to understand the water and effluent systems entailed visiting the individual facility on several occasions and spending days interviewing relevant people and walking the water and effluent systems. Prior to gaining access to an individual facility, health and safety training had to be first carried out. The work to understand the site-specific water and effluent systems took approximately 18 months.

3.5.1 Water and Effluent Performance

Table 3.7 gives a summary of water and effluent performance within all the Port Talbot Steelworks' 8 facilities in m³/tonne of the product in question.

Table 3.7 Water related performance of Port Talbot Steelworks' facilities

Facility	tonnes product / year	Water intake / m³ /annum	Water discharge m³ /annum	Water intake / t of product	Water discharge / t of product
Cokemaking	990 392	2,462,000	1,147,500	2.48	1.16
Sintering	3 875 060	315,000	0 (negligible)	0.08	0
Blast Furnace	3 853 757	8,500,000	1,988,500	2.20	0.26
BOS	4 413 900	1,700,000	1,401,600	0.39	0.32
Casting	4 276 765	4,400,000	1,138,800	1.03	0.27
Hot Rolling	3 051 801	3,504,000 (67,802,400)	0 (64,824,000)	1.15 22.22	0 21.24
Cold Rolling	1 085 833	1,289,000	604,440	1.19	0.56
CAPL	741 657	257,000	78,840	0.35	0.11

A detailed description of the water and effluent systems of some of the most important individual facilities, including Coke-Ovens (Section 3.5.2), Sinter Plant and Material Handling (Section 3.5.3), Blast Furnaces (Section 3.5.4), BOS Plant (Section 3.5.5), Continuous Casting Plant (Section 3.5.6) and Hot Mill (Section 3.5.7) now follows.

3.5.2 Coke-Ovens Water Systems

Large quantities of water is used at the Morfa Coke-Ovens for the quenching of hot coke, for cooling and for the washing of the gas produced from the battery ovens.

Water is also used for fire hydrants, cooling on the batteries and for cooling in the cascade coolers and re-circulating cooling towers. Water is further used at the coal stockyard for dust suppression (Energy Department, 2002).

During quenching some 22 tonnes of water is dropped onto to every coke batch and out of this, about 10 tonnes is recovered as hot water back to the settling ponds, where the coke breeze material drops out. Contaminant-free water must be used for quenching, as any contaminants would be spread to the environment by the quench plume, which has a very high thermal buoyancy (EIPPCB, 2001a). The factors to be taken account in quenching include:

- The use of process-water with significant organic load (like raw coke oven wastewater, wastewater with high content of hydrocarbons, etc.) as quenching water is to be avoided (EIPPCB, 2001a) and
- The amount of water used for quenching combined with the quenching time (including design and efficiency of the quench tower and coke car) should be optimal.

The main effluent from coke-ovens is born during cooling and washing of the coke-oven gas, which is generated during the operation of the by-product plant, removing the impurities of the coke-oven gas by stripping. The coke-oven gas washing effluent has a temperature of 30-35 °C and following impurities: phenol. Cyanide, ammonia, benzene, PAHs, SS, etc.

The required gas washing effluent treatment requires several steps, including:

- Wastewater pretreatment by:
 - Efficient ammonia stripping, using alkalis. Stripping efficiency should be related to subsequent wastewater treatment. Stripper effluent NH_3 concentrations of 20 mg/l are achievable and
 - Tar removal (EIPPCB, 2001a).
- Wastewater treatment by (EIPPCB, 2011a):
 - Biological wastewater treatment with integrated nitrification/denitrification achieving:

- COD⁴ removal: >95%, corresponding to 150 mg/l
- BOD⁵: <20 mg/l
- sulphite <0.1 mg/l
- PAH⁶: <0.02 mg/l
- SCN⁻: <4 mg/l
- CN⁻: <0.1 mg/l
- phenols: <0.5 mg/l
- sum of NH₄⁺, NO₃⁻ and NO₂⁻: <30 mg/l
- suspended solids: <40 mg/l

The above concentrations are based on the specific wastewater flow of 0.4 m³/t of coke.

3.5.2.1 Coke-Ovens Water Supply and Consumption

Presently, the Morfa Coke-Ovens water supply system is insufficiently metered and therefore a water mass balance has been built based on estimates from the cooling towers, heat exchangers and quenchers. As can be seen in the water mass balance Figure 3.29, the Morfa Coke-Ovens uses some 281 m³/hour or 2,461.560 m³/annum.

This service water is abstracted from the Works Reservoir (Figure 3.29) and the main users of the water in the Coke-Ovens include:

- Battery quencher ~54 m³/h – evaporated,
- Benzole Plant direct cooling water ~134 m³/h,
- Recirculating cooling system ~93 m³/h – 71 m³/hour is evaporated and
- Coal Yards dust suppression ~4 m³/h.

⁴ Chemical Oxygen Demand

⁵ Biological Oxygen Demand

⁶ Polyaromatic Hydrocarbons

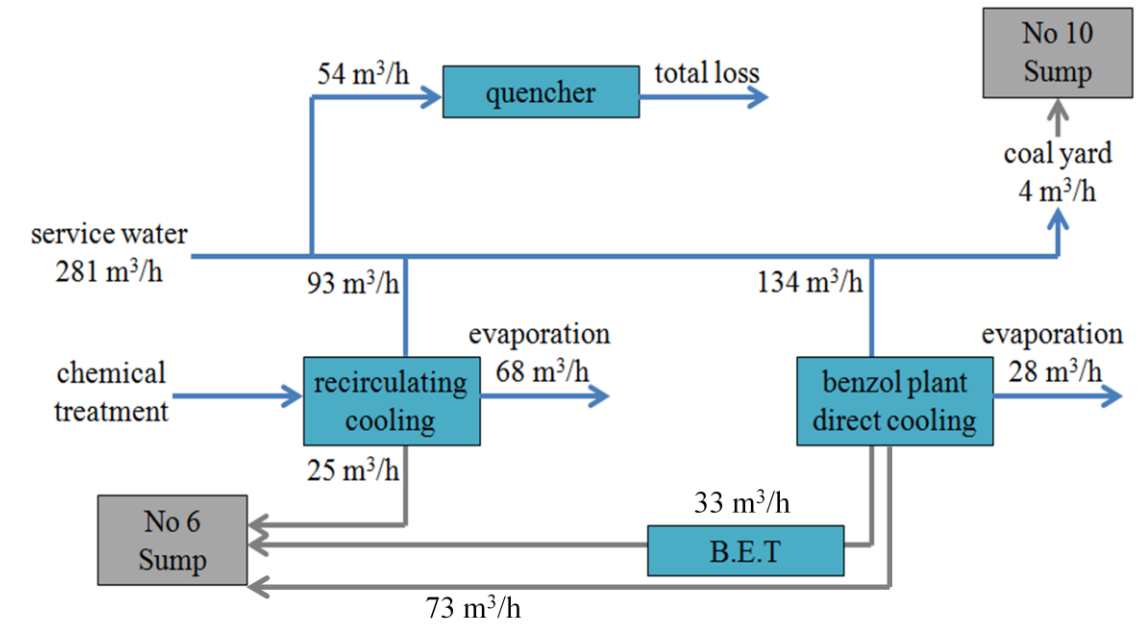


Figure 3.29 Morfa Coke-Ovens water mass balance (adapted from Denley, 2007)

3.5.2.2 Coke-Oven Effluent Water and Effluent Pollutants

There are two basic types of effluent water produced during the carbonisation and classification of fuel:

- Waste formed during cooling and washing the gas and
- Waste formed during the purification of by-products (Ghose, 2001).

In the Morfa Coke-Ovens approximately 131 m³/hour or 1,147,500 m³/annum of effluent water is generated with the main effluent producers being:

- Recirculating cooling system blow down ~25 m³/hour and
- Process cooling water (including biological effluent treatment plant) ~106 m³/hour.

As can be seen in Figure 3.29, most of the effluent born in the Coke-Ovens is discharged to Sump No. 6. The water that is used for dust suppression in the coal stockyards and haul roads in the Coke-Ovens area, in times of dry weather, together with any excess stormwater is collected to the Coalhandling Sump. In the Coalhandling Sump, coal solids are removed from the effluent water, after which the water is sent to Sump No. 10 of the Steelworks' effluent system.

The key water pollutants from the coke-oven operations include: phenol, cyanide, ammonia, oil and grease and suspended solids (Yoon-Gih Ahn, 2006). The most heavily polluted effluent liquor from the coke-ovens is the effluent water from the ammonia stills of the by-product plant. This is where the gas washing and virgin liquor from the gas coolers is processed through the ammonia stills. The still effluent contains ammonia, phenol, cyanide and sulfide, which are toxic to aquatic life (Ghose, 2001). The still effluent that originates as a by-product when the coal is charged to the Coke-Ovens is treated at the Biological Effluent Treatment (B.E.T) Plant. The B.E.T Plant removes much of the organic components and cyanides. After the B.E.T this water is sent to clarifiers from where it is sent to Sump No. 6 as seen in Figure 3.29.

The B.E.T plant was commissioned in 1981 and it includes aerators that use an activated sludge process. In 1986 a Vitox activated sludge system was added in order to reduce the energy consumption of the aeration tanks, but the original aerator system was taken back to use in 2002.

3.5.3 Sinter Plant and Raw Material Handling Water Systems

The operations of the Sinter Plant in Tata Port Talbot Steelworks consist of two main parts; the actual sinter plant and the 'raw material handling', which includes the harbour and the ore preparation plant. In raw material handling, water is being used for cleaning the ships, adding weight to the ballast tanks as well as for dust suppression of material stockpiles and stockyard roads. The total volume of water used at the raw materials handling area is small compared to other manufacturing areas on site. This is also the case for the Port Talbot Sinter Plant, where most of the water is being consumed to control moisture levels in the raw mix feed.

3.5.3.1 Sinter Plant and Raw Material Handling Water Supply and Consumption

The average water consumption for a sinter plant is estimated to be some 0.01-0.35 m³/t of ready product (EIPPCB, 2001a). Port Talbot Sinter Plant is producing 3,875,060 tonnes of sinter per annum and therefore the annual water consumption could be anything from 38,751 m³ to 1,356,000 m³.

As can be seen in Figure 3.30 most of the water used at the Sinter Plant is service water from the Works Reservoir.

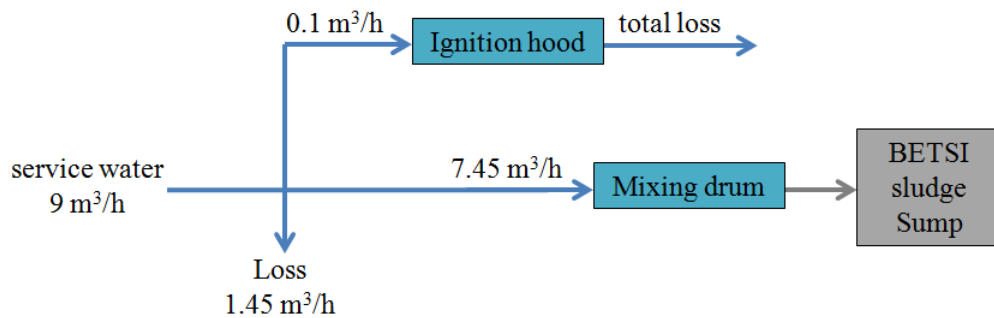


Figure 3.30 Sinter Plant water mass balance

At the present time, the Sinter Plant service water system is insufficiently metered; fortunately there are consumption figures available for the mixing drum, which is by far the main consumer of water at the site. Based on the 2 hourly consumption figures, some 7.45 m³/h or 65,000 m³/annum is used in the mixing drum. After the mixer, the moisture level of the sinter is some 5-5.8%. Jenkins (2007) estimates that the raw water mixer covers some 90% of the total Sinter Plant water consumption, with the remaining ~10% being used mainly for dust suppression at the conveyors. Cooling water is used for the cooling of the ignition hood. This cooling system is closed with the water being recycled back to use and requires only some 0.1 m³/h of make-up water. There's also an additional ~0.5 m³/hour loss on the systems, giving the Sinter Plant a total consumption of approximately 9 m³/h or ~80,000 m³/annum.

The main water source to the raw material handling is the dock water. Most of the dock water used in the steelworks is used for cooling purposes and after use the water is recycled back to the dock. Most of the make-up water required for the dock is received from the Ffrwdwyllt River, but at times of low water flows in the river, water is abstracted from the River Afan mouth. The water at the River Afan mouth tends to have brackish water, which is why the docks water has sometimes increased salinity levels.

Altogether, around 27 m³/h or 236,500 m³/annum is being used at the raw material handling area (Figure 3.31). The water used at the raw material handling includes:

- ~1.8 m³/h or ~16,000 m³/annum on roads

- $\sim 24 \text{ m}^3/\text{h}$ or $\sim 210,000 \text{ m}^3/\text{annum}$ on ship unloading and
- $\sim 0.7 \text{ m}^3/\text{h}$ or $\sim 4,000 \text{ m}^3/\text{annum}$ on stockpiles

It should be noted that there have been problems with the leaks on the water mains running to the Port Talbot Sinter Plant and raw material handling due to the old supply pipe network. The service water main has been recently renewed but this hasn't removed all the problems (Maynard, 2008).

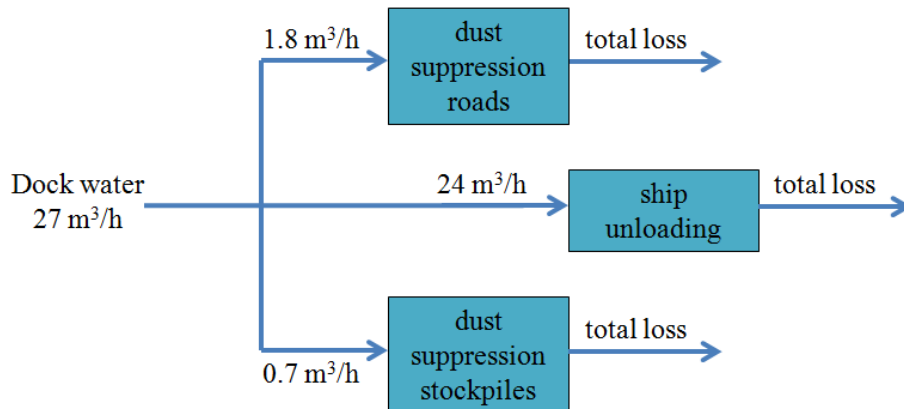


Figure 3.31 Raw Material Handling water mass balance

3.5.3.2 Sinter Plant and Raw Material Handling Effluent Water and Pollutants

Most of the water used in raw material handling will evaporate or remain within the raw materials, whilst any excess will go to soak ways and drains. At this stage, some solids will be entrained (Jenkins, 2007). Also, the dust suppression by water on the roads and premises etc. results in a run-off wastewater containing suspended solids (including heavy metals), which are the main pollutants from the sinter plant operation (Yoon-Gih Ahn, 2006). For a sinter plant producing some 11,000 tonnes of sinter per day, the rinsing water flow is $\sim 460 \text{ m}^3/\text{day}$ (EIPPCB, 2001a). With the average 12,000 tonnes production of Tata Port Talbot Sinter Plant per day, the usage of rinsing water can be expected to be some $500 \text{ m}^3/\text{day}$ or $20.8 \text{ m}^3/\text{h}$.

There are currently no specific on-source water treatments in place at the burdening section, but the wastewater is sent to the 'Betsi Lagoon' together with the Blast Furnaces slurry.

3.5.4 Blast Furnaces Water Systems

Blast furnaces are water intensive in nature, but due to the possibility of using close-circuit water systems and reusing effluent water, the difference in water consumption from one furnace to another can be considerable and the average consumption of water in blast furnaces within the EU is estimated to be between 0.8 and 50 m³/t pig iron (EIPPCB, 2001a). The Port Talbot blast furnaces produced some 3.855 Mt of iron in 2007 and therefore, the expected water consumption could be anything between 3.1 and 192.8 million m³. The water use at the Port Talbot blast furnaces area can be divided into main categories of:

- Blast furnace cooling (No. 4 and 5)
- Blast furnace gas washing (No. 4 and 5) and cooling
- Slag granulation and
- Slag quenching (Maynard, 2006).

3.5.4.1 Blast Furnaces Water Supply and Consumption

The blast furnace water systems are complex with a number of different types of water being consumed for several purposes. Most of the water used in the blast furnaces is needed for several cooling purposes. Rivers Afan and Ffrwdwyllt are both supplying water to the blast furnaces. Both of the rivers feed the open circuit cooling (OCC) systems, the gas cleaning operations as well as slag quenching (Energy 2002 & 2005). The River Afan feeds 171 m³/h or 1.5 million m³ per annum, whereas the River Ffrwdwyllt feeds some 84 m³/h or some 735,000 m³/annum to the Blast Furnaces water systems.

Dock water is supplied to Blast Furnace No. 4 via Margam 'B' Power Plant, which plays an important role in supplying water to the blast furnaces. Dock water is used for several purposes including hearth cooling, gas washing and cooling, slag granulation and quenching and make-up for the OCC systems. The Blast Furnaces overall Dock water consumption totals 685 m³/h or approximately 6 million m³ of water per annum, as can be seen in Figure 3.32. Around 90% of the Dock water used is returned back to the Dock and the rest is lost via evaporation. Margam 'B' also supplies water to the

water tower, which is used in case the Margam 'B' pumps fail (Cross, 2008). The water in the water tower holds 30 minutes supply of water to allow for the blast furnaces to be shut down safely.

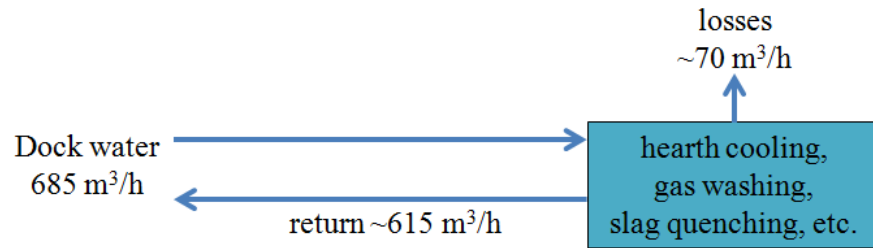


Figure 3.32 Blast Furnaces Dock water mass balance

In addition to the rivers and the Docks abstraction, approximately 25 m³/h or 219,000 m³/annum of service water from the Works Reservoir is used at the blast furnaces for coal injection fire hydrants, compressor cooling and slag granulation (Energy Department, 2005). Additionally, a small amount of soft and de-mineralised (demin) water is used on the blast furnace area. The Abbey soft (from Afan River) water is used as a make-up for the closed cooling circuit at a rate of some 1 m³/hour per furnace equaling 175,000 m³/annum (Maynard, 2008). Estimated de-mineralised water consumption is ~2 m³/day or some 730 m³/annum. Based on the above, it can be concluded that the overall water consumption of the Port Talbot Steelworks Blast Furnaces totals approximately 968 m³/hour or 8.5 million m³/annum.

The water cooling systems on both furnaces are almost identical although each furnace has its own dedicated pumps and cooling circuits. There are two systems of Open Circuit Cooling system (OCC) and Closed Circuit Cooling system (CCC) employed on each furnace (Energy Department, 2002). The OCC uses water from the Afan and Ffrwdwyllt rivers, feeding water to the tuyeres, the big coolers, the hearth and the cone sprays. OCC water is also used as secondary cooling water for the stove heat exchangers as well as providing cooling and flushing water for the BLT gearboxes. Further, in an emergency situation, OCC water is used directly to cool stove Hot Blast Valves or Furnace CCC system coolers. At Blast Furnace No.5 solely, OCC water is used as secondary water for cooling the CCC water in plate heat exchangers. At No.4 furnace, electrically driven fans carry out this function. When required, OCC is also used for leak detection on the CCC system. The CCC system cools the rest of the

furnace i.e. all the stacks and the bosh plate coolers, the tuyeres and the tapholes stove coolers as well as the underhearth cooling pipes (Energy Department, 2002). The make-up water for Blast Furnace number 4 OCC comes from the Afan and Ffrwdwyllt Rivers and the Docks, whereas number 5 OCC is fed preferentially only by the two rivers (Cross, 2008).

After cooling, the water is sent back to the Energy Department, filtered and stored in the cooling towers until it is sent back to the blast furnace for re-use. Soft water is used as a make-up for the CCC systems whereas river or dock water is the make-up for the OCC systems (Energy Department, 2002).

3.5.4.2 Blast Furnaces Effluent Water and Effluent Water Pollutants

Depending on the steelworks, estimated wastewater production for a blast furnace can vary between 0.1 and 3.3 m³/t of liquid iron, while the most important wastewater emission sources are effluent from the blast furnace gas scrubbing, wastewater from slag granulation and blow down from cooling water circuits (EIPPCB, 2001a).

The gas scrubbing effluent contains suspended solid particulates, zinc and other volatile metals, such as lead (Table 3.8), which dissolves in the CO₂ enriched water forming soluble compounds.

Table 3.8 Blast furnace top gas scrubbing effluent parameters (EIPPCB, 2011a)

Parameter	Concentration (mg/l)
CN	0.1-50
Cl	73.6
F	1.74
SO₄²⁻	42
NH₄	2-200
S	0-5
Pb	0.01-5
Zn	0.1-29.36
Fe	6.77
Mn	0.48
Phenols	0.1-5

Water from the blast furnace gas scrubbing is normally treated, cooled and recycled to the scrubber. Treatment itself usually takes place in circular settling tanks. The estimated water overflow of a gas scrubbing plant circuit is 0.1-3.5 m³/t pig iron depending on raw material quality/specification and water availability, which influences the measures available to optimise water recycling (EIPPCB, 2001a).

The layout of the Blast Furnace Gas Scrubbing (gas washing) Plant can be seen in Figure 3.33. The water from the gas washing system is carried to clarifiers where an anionic polymer is added to aid dust settling. Around 50% of the original effluent is recycled back through the gas cleaning system, whilst the remainder is pumped to No. 1 Sump (Swindley, 1999). The settled slurry from the clarifiers is then pumped to the Betsi lagoon and the run off water from the slag quench pools is also pumped untreated to the satellite Sump No. 1.

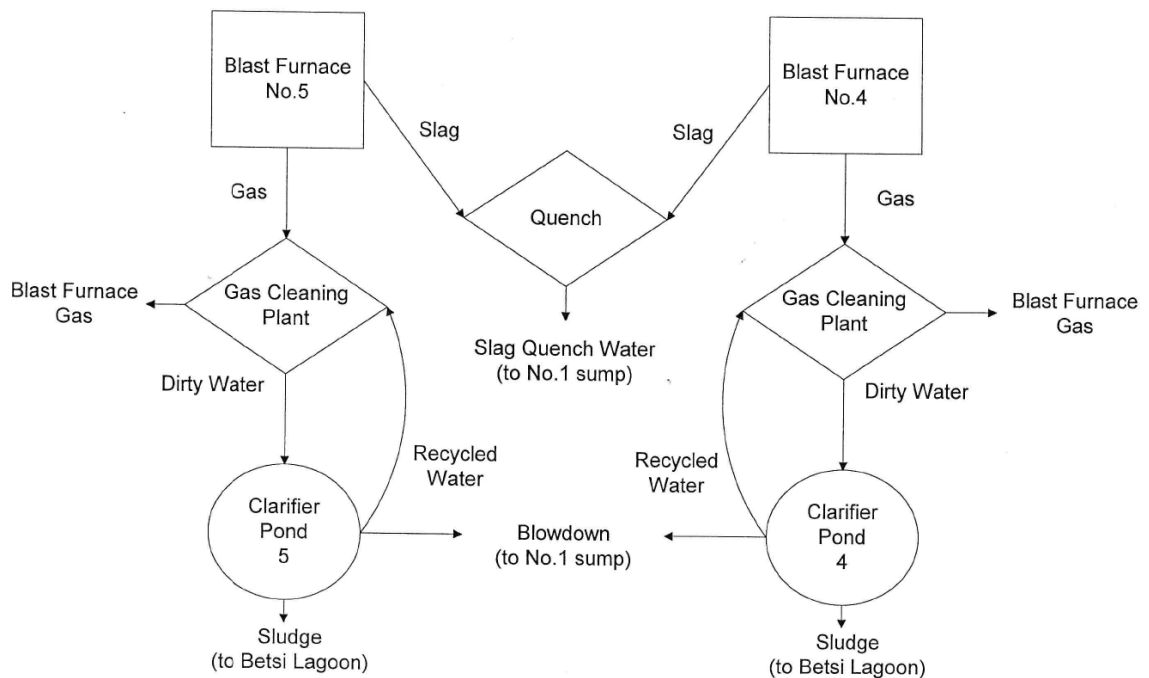


Figure 3.33 Layout of the Port Talbot Blast Furnace gas washing water treatment plant (Swindley, 1999)

The Betsi Lagoon has 3 sections to it. At any given time one of the sections is accepting slurry, one of the sections is drying the excess water from the slurry and the last one is reclaimed. The Sinter Plant uses the slurry after it has been dried at the Betsi Lagoon. The excess water from the Lagoon flows into a reed bed that sits next to the

Lagoon (Energy Department, 2002). The overflow from slag granulation primarily depends on water availability and is estimated to be between 0.125-10 m³/t pig iron produced. The most important pollutants in slag granulation overflow water include: Zn, Cu, Ni, Pb, Cr, COD and TOC (EIPPCB, 2001a).

In the Port Talbot Steelworks Blast Furnaces, the water used in slag granulation is running on a closed loop and even though there is evaporation through steam generated in the process, there is no actual effluent discharged from it. After usage in the slag granulation process, the water is run through a de-watering sump to a cooling tower to be re-used in the process (Cockins, 2008).

The only effluent flow generated from the cooling circuits is the blow down, although there are heavy losses through evaporation within the open cooling water circuit. After the cooling process, the remaining water from the open circuit cooling circuit is filtered and returned via the Margam 'B' Power Plant back to the blast furnace to be re-used in the process (Maynard, 2008).

The total effluent water generated during the blast furnace operations was 227 m³/h or 1,988,500 m³/annum in 2008 (Figure 3.6). Most of this effluent is generated during gas cleaning and slag quenching activities.

3.5.5 BOS Plant Water Systems

A Basic Oxygen Steelmaking plant requires an estimated 0.4-5 m³ of water per tonne of liquid steel (EIPPCB, 2001a). The Port Talbot BOS Plant produced some 4.1 Mt of liquid steel in 2006 and therefore the expected water consumption could be anything between 2 million m³ and 20.5 million m³ per year. There are several water consumers in a basic oxygen steelmaking plant including:

- Oxygen lance cooling – Often by re-circulating cooling water system.
- Hood cooling – Usually cooled with water re-circulating through the hood panels.
- Gas cooling and wet scrubbing system – This water is then sent to clarifier-thickeners for sedimentation of the solids, and water can later be recycled or discharged (Nalco, 1988).

- Degasser vessel cooling – Water is used for cooling the flanges and lances (Energy Department, 2002).

3.5.5.1 BOS Plant Water Supply and Consumption

Not only does the BOS Plant of Port Talbot Steelworks use considerable amounts of water, it uses fairly large quantities of more expensive, pretreated soft and demineralised water. In the BOS Plant, the hood and lance cooling and degasser vessel cooling systems use a combined $\sim 45 \text{ m}^3/\text{h}$ or $\sim 400,000 \text{ m}^3/\text{annum}$ of soft water as a top-up.

The hood and lance cooling closed re-circulating system uses soft water from the Abbey water treatment plant as the main top-up supply with a little service water being added to increase calcium levels at the system. The service water acts as an emergency top-up supply in case there are problems with the soft water supply. The soft water used in the cooling system is treated with inhibitors both to control the corrosion of the internal pipe infrastructure and the amount of bacterial activity. The hood and lance cooling system has an open cooling tower, which accounts for most of the losses together with the blown down water from the system (Energy Department, 2002; Mainwaring, 2008).

During the BOS converter blowing cycle, large quantities of dust laden fume is produced. An induced draught fan extracts the fume through the gas cleaning plant, where the dust is separated from the gas using water sprays and venturi scrubbers (Chu, 2008). Clarification and filtration is used to remove the majority of solids and dusts from the system. Large proportions of the dust collecting water is recycled back to the system after use (Chu, 2008), while some $2 \times 24 \text{ m}^3/\text{h}$ of service water, equaling $\sim 420,000 \text{ m}^3$ of water per annum, is added to the system as a make-up water (Energy Department, 2002 & Mainwaring, 2008). Apart from gas cleaning and washing system, service water is used in several systems in BOS Plant, including as a bleed to cooling tower, as scrubber water, for the fan coolers, as a converter seals, under the demister, for dust collection and for the water tank (Water Experts Team, 2006). Altogether an estimated $125.5 \text{ m}^3/\text{h}$ or 1.1 million m^3 of service water per annum is consumed at the BOS Plant

The degasser vessel cooling is used for cooling the flanges and lances at the BOS vessel. The degasser vessel cooling water runs in a closed circuit system with cooling towers. Approximately 200,000 m³ of soft water from the Abbey Water Treatment Plant is used as make-up water in order to top-up the closed system due to losses resulted via evaporation in the system and blowdown from the cooling tower. The water used at the degasser vessel cooling is treated with inhibitors to minimise internal corrosion and bacterial activity (Energy Department 2002, Water Experts Team, 2006).

3.5.5.2 BOS Plant Effluent and Effluent Water Pollutants

The most important sources of wastewater in the BOS and continuous casting plants include scrubbing water from the BOS gas treatment and water from the direct cooling in continuous casting (EIPPCB, 2001a).

BOS gas effluent treatment is very often performed in two steps of separation of coarse particles (>200 µm grain size) followed by sedimentation in circular settling tanks. Flocculating agents are added to improve sedimentation. The sludge is de-watered by means of rotary vacuum filters, chamber filter presses or centrifuges (EIPPCB, 2001a).

In Port Talbot Steelworks' BOS Plant, after the gas cleaning operation, the dust laden water is sent to the gas washing water treatment plant shown in Figure 3.34. The dust collecting water from the gas cleaning plant is conveyed in a flume to the inlet of the water treatment plant. The de-gritter settles heavy grit from the water and the settled grit from the bottom of the tank is removed by a chain driven scraper. From there, the water flows into the clarifier via a splitter box where a flocculating polymer (poly-electrolyte) is added. The clarifier pond has a four arm rake that scrapes the settled sludge into the centre of the clarifier. The sludge is then pumped to the filter press filter by using a diaphragm pump. The rotary vacuum filter dewateres the sludge and discharges the filter cake onto a conveyer belt. The clarifier then overflows to a pumping pool and some of the water, containing some solids, is blown to Sump No. 5 and further from there to the steelworks' effluent system (Energy Department, 2002 & Swindley, 1999).

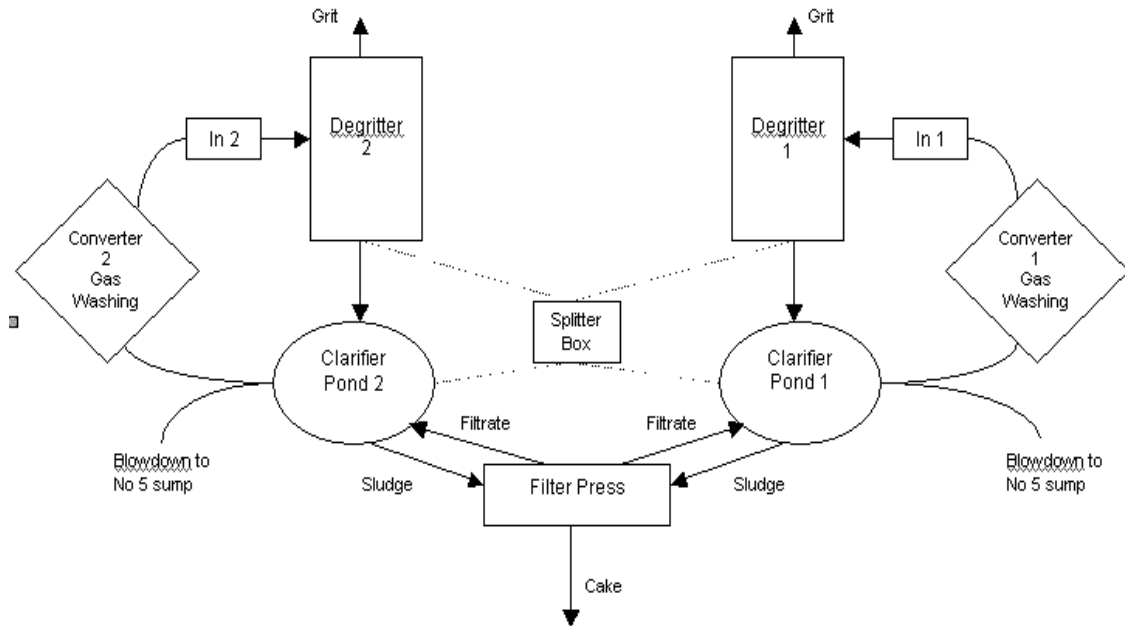


Figure 3.34 Layout of the Port Talbot BOS gas washing water treatment plant (adapted from Swindley, 1999)

There is also some effluent water born as blowdown from the cooling tower of the hood lance and sub-lance cooling systems and degasser vessel cooling system (Water Experts Team, 2006).

The total volume of effluent generated during BOS Plant operations is approximately 160 m³/h or 1.4 million m³/annum and most of it arises during the gas cleaning activities.

3.5.6 Continuous Casting Water Systems

Correct water treatment and distribution is critical to continuous casting. In the process, steel that is leaving the BOS ladle at about 1550 °C is poured into a tundish, from where the molten steel is distributed to form slabs in the mould. The mould is a copper jacket, water-cooled in order to provide high heat exchange rates. As the cast starts, the cooling effect of the water-jacketed mould (Figure 3.35) starts the formation of a metal skin. Proceeding through the length of the mould, the skin-contained metal is exposed to a series of direct-contact water sprays, which complete the job of solidifying the steel. The crucial point in this process is the copper water-cooled mould, which forms the

initial skin. Unless the skin is formed quickly and uniformly, a breakout will occur, that will shut down the whole operation (Nalco, 1988).

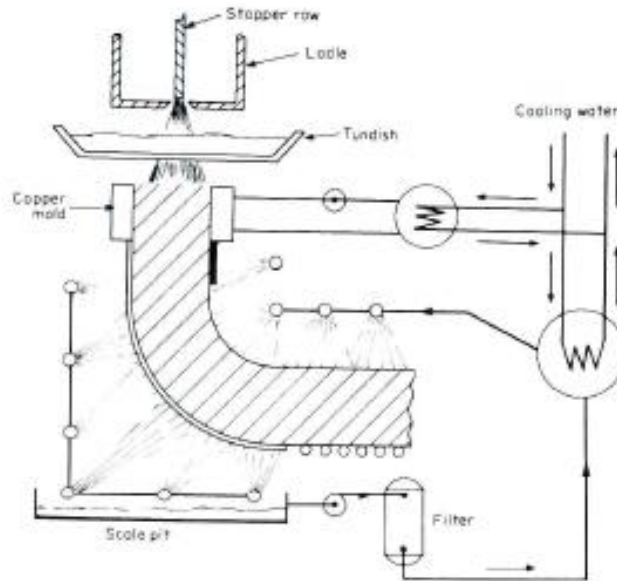


Figure 3.35 Cut view on cooling water application during continuous casting of slabs (Nalco, 1988)

The main water consumers in a continuous casting plant include mould cooling, slab spray water and machine (roll) cooling water (Energy Department, 2003). The most reliable cooling water program for the mould cooling uses the highest quality water available in a closed loop, as the hardness levels should never exceed 10 mg/L of minerals. Since the system is closed, there is little loss and the best corrosion inhibitors and dispersants can be used. Spray water that contacts the slab becomes contaminated with iron oxide particles as the hot metal is oxidised. The water is processed in a filtration system for solids removal, recirculated through heat exchangers and recycled to the sprays. The sprays must be kept from plugging at all times because the flow of water to the slab being cooled must be uniform at all points (Nalco, 1988).

3.5.6.1 Continuous Casting Water Supply and Consumption

A great amount of water is used for cooling at the continuous casting plant. Further, in order not to interfere with the high grade of steel slabs, cooling water used in some of the continuous casting processes, including coolant for moulds and rolls, needs to be pretreated de-mineralised or soft water. The estimated overall water consumption of the

Continuous Casting Plants 1, 2 and 3 is a staggering 502 m³/h or 4.4 million m³/annum. Out of this, an estimated 1.0 million m³/annum of water used is pretreated de-mineralised and soft water, 3.4 million m³/annum comes from the River Afan and 1.1 million m³/annum from the Works Reservoir as service water.

A high quality water system is required for the cooling of the moulds, rolls and bearings of the casting machines due to the high rates of heat transfer occurring at the process. The importance of a high standard cooling system is further stressed by the possibility of losing a whole caster of hot metal in the event of a breakdown failure (Energy Department, 2002).

In all the 3 casting machines, the mould and machine cooling each have a dedicated 'semi-closed' cooling primary circuit, while they're all sharing a common secondary circuit that works as a back-up supply. The primary systems circulate water from a closed concrete holding tank, through the machine or mould to a plate type heat exchanger, returning to the holding tank. Each primary system has an emergency header tank, which has sufficient capacity to maintain supply in the event of the failure of the pumped circuit (Energy Department, 2002; Mainwaring, 2008). The types of water used at the different casters for primary and secondary cooling systems with estimated figures for consumption are:

Caster 1 systems

- | | |
|------------------------------|------------------------|
| - Primary mould: demin water | 2 m ³ /h |
| - Primary roll: demin water | 4-10 m ³ /h |
| - Secondary: soft water | 29 m ³ /h |

Caster 2 systems

- | | |
|--|-----------------------|
| - Primary mould: demin water | 2 m ³ /h |
| - Primary roll: soft, demin and Afan River water | 25+ m ³ /h |
| - Secondary: soft water | 36 m ³ /h |

Caster 3 systems

- | | |
|------------------------------|------------------------|
| - Primary mould: demin Water | 2-10 m ³ /h |
| - Primary roll: soft water | 2-10 m ³ /h |
| - Secondary: soft water | 36 m ³ /h |

(Water Experts Team, 2006; Mainwaring, 2008)

The softened (soft) and demineralised (demin) water used in the three casters as a make-up to the cooling systems is provided by the Abbey Water Treatment Plant, alternatively clarified River Afan water is also used. Caster 2 and 3 secondary cooling systems are open-cooling tower systems, circulating through the plate coolers and are subject to normal evaporation and blow down losses (Energy Department, 2002; Water Experts Team, 2006).

Further to the mould and roll cooling, the continuous casting system requires water for spray cooling directly onto the surface of the rolls, the machine itself and the casting slabs. In Port Talbot the spray cooling of caster 1 and 2 use Afan River water with service water as a back-up, where as Caster 3 uses service water as its main source of spray cooling water (Water Experts Team, 2006; Mainwaring, 2008). The types of water used at the different casters by the spray cooling systems with estimated figures for consumption are (Water Experts Team, 2006):

- Caster 1: Afan River water 140 m³/h,
- Caster 2: Afan River water 150 m³/h and
- Caster 3: Service water 125 m³/h.
-

Prior to use, the spray cooling water is pretreated. The water runs through rotary screens to remove the organic debris followed by a clarifier that allows the flocculants of the suspended solids to form sludge. The cleaned water then passes to a further holding/treatment tank, one for each of the continuous casting plants. The clarified waters are then sent to top up the holding tank or the cooling tower cold well and then pumped to the cooling sprays (Water Experts Team, 2006; Mainwaring, 2008), from where there is a loss of 60 m³/hour through evaporation (Water Experts Team, 2006). The overflow from the clarifier is pumped into a bank of sand filters which remove fine solids, grease and some oil from the flow. The sand filters are prone to progressive blinding, accelerated by the grease content, and require frequent back-washing to maintain performance. Next to the cooling and spraying, considerable amounts of water is used in the Casters for backwashing the sand filters (Mainwaring, 2008 & Acqua/Baemar Howells, 2008).

3.5.6.2 Continuous Casting Effluent and Effluent Pollutants

Within continuous casting, effluent is generated by the direct cooling system, especially the spray cooling system. The discharge water born in the direct cooling process is contaminated with metal oxides (suspended solids) and with hydrocarbons (oil) (EIPPCB, 2001a).

The effluent spray cooling water from Caster 1 is discharged 14,000 L/minute (840 m³/h) into a 'hydrocyclone', which removes the coarse mill scale and other large suspended solids. The scale-free water then flows over the weir into a sump before being pumped through sand filters before being returned to the sump. The sand filters are then backwashed with water that removes all the sediment remaining after the effluent water treatment. Water used for backwash is then pumped to the effluent plant's clarifiers and from there, after treatment, to the Continuous Casters Sump. The spray cooling water from Casters 1 and 3 is discharged to settling tanks to drop off the suspended solids, with the help of a coagulant from where it is discharged to the Continuous Caster Sump which is part of the Steelworks effluent system (Sullivan, 2008).

3.5.7 Hot Mill Water Systems

There are a number of different water systems in use within the Hot Mill, each having a different quality (cleanliness) and pressure. The three main types are called 'service' water, 'descaling' water and 'roll coolant' water system (Figure 3.36).

All the water used within the Hot Mill originates from the Works Reservoir and is so called service water, but prior to use the descaling and roll coolant water is subjected to a single pass through sand filters. The service water is not pretreated apart from being run through screens. Roll coolant water is of the highest quality, followed by descaling water, with service water being the lowest quality water. Water pressures for the three systems are typically 3.5 bar for service water, 8-10 bar for roll coolant water and 150-180 bar for the descaling water (Morris, 2009).

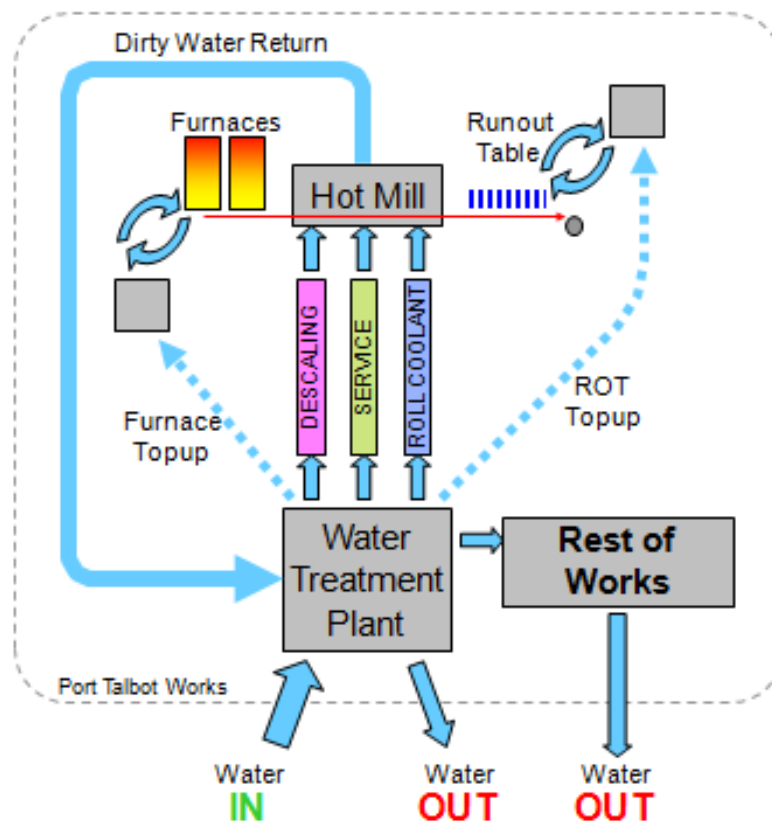


Figure 3.36 Overview of the Hot Mill water systems (Morris, 2009)

3.5.7.1 Hot Mill Water Supply and Consumption

The total Hot Mill water usage includes 4460 m³/hr for the roll coolant, 2560 m³/hr for service water and 360 m³/hr for descaling or in proportions 60%, 35% and 5% for roll coolant, service and descaling water respectively (Morris, 2009).

The Hot Mill itself is divided into 4 different sections of:

- Furnaces and roughing,
- Finishing mill and coiling,
- Reheat furnaces system and
- Run out table system.

All the sections of the Mill use water in several applications, a simplified layout of the Hot Mill water systems gives an idea of what routes different types of water take and how they are treated (Figure 3.37).

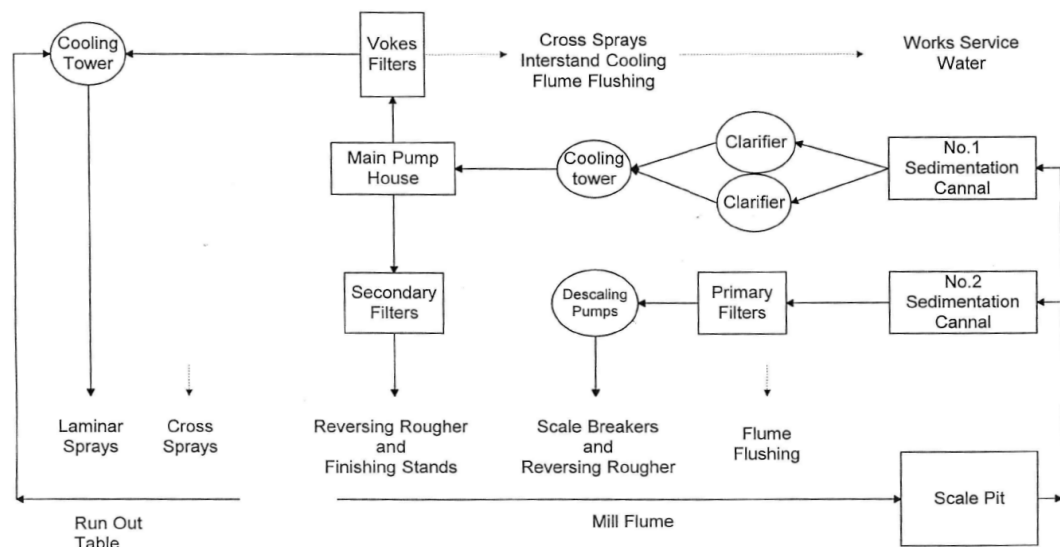


Figure 3.37 Layout of the Hot Mill water system (Swindley, 1999)

There are a number of water applications within the finishing mill. On the coil entry side, there are scrubbers that spray high pressure service water directly onto the strip. There are also edge sprays on these first three stands' entry guides on both top and bottom of the strip as the edge is shielded from the scrubbers' water by the edge guides. On the exit there are interstand cooling headers that consist of headers with a transverse slot along their length, which puts a curtain of service water onto the strip to chill its surface. All seven of the Finishing Mill stands have multiple roll cooling headers to cool the surfaces of the work rolls, fed from the roll coolant system. The supply of adequate cooling uses most water within the Hot Mill. This water is of the highest cleanliness and has its own dedicated water supply system, i.e. apart from the Crop shear it is only used for Finishing Mill roll cooling (Morris, 2009).

When the strip comes out of the Finishing Mill, its thickness is checked with an x-ray gauge, which is cooled by service water. From here the strip travels to the Run Out Table (ROT), which consists of multiple cooling banks on top and underneath the strip, that spray ROT water onto the surfaces to remove heat in order to control correct metallurgical properties. As can be seen in Figure 3.37, this re-circulating water system has its own cooling towers to control the temperature of the water used. The Run Out Table cooling water has a tendency to pool on the strip surface and in order to clear that,

cross sprays are mounted along the operator side of the Run Out Table that spray service water across the strip and thus clear the warmed water off the strip ready for the next cooling bank. After cooling, the finished strip is coiled by one of two coilers which are themselves kept cool with service water (Morris, 2009).

The Reheat furnaces have their own closed-loop re-circulating water system (Figure 1.39) that is used to cool the walls, roof, doors, and walking beam system. Water stored in the main holding tank is pumped through two filters and then to the furnaces. When it returns, it is cooled in one of three cooling towers before returning to the holding tank. Once used, this water returns to the dirty water ponds for recycling to the water treatment plant (Morris, 2009).

Like the Furnace cooling, the Runout Table has its own closed-loop re-circulating cooling system (Figure 3.36). Once it drops from the strip, it is collected in the flume under the Runout Table. At the Finishing Mill end of the Runout Table flume is a weir that allows excess water to overflow into the Finishing Mill flume and out to the dirty water return. Cross sprays, are one source of makeup water for losses from the system due to evaporation at the cooling towers and overflows over the weir and take their water from the service water main in the Finishing Mill basement.

3.5.7.2 Hot Mill Effluent and Effluent Pollutants

Water for the various cooling tasks is returned via the Dirty Water Return (Figure 3.36) to be recycled for reuse within the Mill and there are no specific effluent arising within the Hot Mill operations. As seen in Figure 3.37, the used water first passes along the mill flume to a scale pit, where coarse scale is removed and the returned water is then split between No.1 and No. 2 sedimentation canals. Clarified water from No. 2 sedimentation canal is then filtered through the primary sand filters and pumped to the de-scaling pumps, to the cooling tower or it is returned to the main pump house. The Water from No. 1 sedimentation canals passes through further clarifiers before going to the cooling tower and is then returned to the main pump house (Swindley, 1999). Thus, apart from evaporation losses, the vast majority of water used in the Hot Mill is continually recycled to the Water Treatment Plant for reuse. This re-circulation system

however is not closed, as the Water Treatment Plant supplies the entire Port Talbot Works with water. The total flow rate of the Dirty Water Return is $\sim 7400 \text{ m}^3/\text{hr}$ (Morris, 2009) and there is a top-up of $\sim 400 \text{ m}^3/\text{hr}$ for the Hot Mill cooling water systems from Works Reservoir to the Water Treatment Plant, which totals an input of $\sim 7800 \text{ m}^3/\text{hr}$ to the Hot Mill water systems.

3.6 Conclusion

Due to a long operational evolution of the Tata Port Talbot Steelworks, the works' water supply and distribution systems have evolved into a complex and extensive system with several abstraction points, an extensive pipe network and several water and wastewater treatment plants.

A huge amount of around $145,020,000 \text{ m}^3$ (2007) per annum of water is being used in the Steelworks over a year. $>88\%$ of this is abstracted from the Docks and used mainly for indirect, once-through cooling purposes. Of the water used, around $12,500,000 \text{ m}^3$ is discharged annually via the Long Sea Outfall. Out of a total effluent, around $3,500,000 \text{ m}^3$ per annum is treated by the Nautilus final effluent treatment plant in order to remove suspended solids, particularly zinc, prior to the discharge.

Nautilus chemical precipitation treatment system generally performs well in the removal of suspended solids, although on occasion high levels of zinc cause breaches.

Out of the individual production facilities, most water is used by the blast furnace, although casting and hot mill water consumption levels are also high. The most complex effluents are arisen during coke-oven and blast furnace operation and most of the zinc is present within the blast furnace effluent.

4 WORLDSTEEL WATER MANAGEMENT PROJECT

4.1 Introduction

The World Steel Association (WSA) or worldsteel was founded on 19 October 1967 as a non-profit research organisation with headquarters in Brussels, Belgium. In April 2006, worldsteel opened a second major office in Beijing, China. Worldsteel is one of the largest and most dynamic industrial associations in the world. Worldsteel represents approximately 180 steel producers (including 19 of the world's 20 largest steel companies), national and regional steel industry associations, and steel research institutes. The members of worldsteel produce around 85% of the world's steel output.

The purpose of the association is to provide a forum for the world's steel industry for addressing any strategic issues or challenges it is facing on a global basis. In addition, worldsteel facilitates benchmarking of best practices amongst its members across many aspects of steel manufacturing. The association promotes steel products and industry to customers, other industries, media bodies, and the general public and assists its members to develop the market for steel. Worldsteel also promotes a zero-harm working environment for steel industry employees and contractors.

The use of freshwater as a performance indicator was proposed and data collected for the International Iron and Steel Institute's 2005 Sustainability Report after it was realised that freshwater is a regional issue and the emphasis of issues differs greatly by region (quality, quantity, etc.) whereas the worldsteel (former International Iron and Steel Institute or IISI) sustainability performance indicators are global. Water remained on the agenda of both the worldsteel member companies and the worldsteel itself, and at the 44th meeting of the worldsteel Committee on Environmental Affairs (ENCO-44) in 2006 worldsteel discussed the issue further and decided to form a small group with Sustainability Reporting Project Group's (SRPG) support to look at the issues and scope the project, considering both quantity and quality. It was agreed that a water management project was to be initiated and extra members would be sought from the member companies (IISI, 2007).

This chapter explains the initiation of the worldsteel Water Management Project and Working Group. It describes the background of the project and explains how the benchmarking survey, created as a part of the project, was developed. The author of this thesis worked as one of the long standing members of the group and was one of the members to significantly contribute to the final project report: *Water Management in Steel Industry 2011*. Furthermore, the author contributed majorly in the development of the survey used for gathering data as part of the worldsteel water management project as explained later in the Chapter. The journal articles written by the author about the worldsteel project and its findings can be found at Appendix I.

4.1.1 Aim and Objectives

The IISI Water Management Project was initially launched in order to prepare the steelworks for future public and political pressures relating to water which, together with establishing suitable key performance indicators (KPIs) for the use of the steel industry, is the main aim of the project. Other aims include demonstrating that the sustainability of the steel industry is not being compromised by their approach to water issues and providing best-practice exchange on water management (IISI, 2007).

In other words, the aim was to achieve efficient water management now and for the future by:

- Comparing members' policies and strategies on water management,
- Benchmarking global rates of water use and consumption and
- Evaluating further opportunities for water utilisation and consumption rate improvements by making an inventory of technologies applied.

In line with the project aims, the objectives of the project were to:

- Collect information, facts and material on important water issues for the steel industry in each region of the world, and on what the industry is doing to manage its water resources.
- Include contributions made by the steel industry in providing water for communities in areas of water scarcity.

- Cover all aspects of water issues, including environmental, resource availability, commercial, operational, political, etc.
- Ensure that the industry is prepared for current and expected future public and political discussions on water.

The main deliverable of the project is a report that covers steelworks water-related issues, including:

- Consumption rates,
- Considerations on how water strategy is formulated,
- Identification of state-of-the-art water technologies and practices and
- Evaluation of further opportunities for water utilisation and consumption rate improvement (worldsteel, 2011).

4.2 Project timeline and meetings

The project was launched in 2007, with the first official meeting taking place in June 2007. By this meeting, the nomination process for the initial working group members was completed. Several meetings were supposed to take place during 2008 and 2009, but due to the difficult economic times at the end of 2008 and 2009, meetings were held back and the delivery of the final report was delayed from the end of 2009 to May 2011. In the end, the working group met four times during the project as can be seen in Table 4.1, although 9 meetings were planned at the beginning.

Table 4.1 Project meeting dates and hosts

Date	Location	Host
June 2007	Brussels, Belgium	worldsteel
October 2007	IJmuiden, The Netherlands	Corus
March 2008	Vitória, Brazil	ArcelorMittal Tubarão
March 2010	Brussels & Gent, Belgium	and worldsteel ArcelorMittal

4.3 Project team

Mr. Hans Regtuit, Tata Steel has been the chairman of the project group and Ms. Åsa Ekdahl, worlsteel has had the role of the project manager. The project group has been made up of the following companies and associations (the names in bold participated to the re-launch of the survey): **ArcelorMittal**, Baosteel, **Blue Scope**, **China Steel**, **CMC**, **Corus**⁷, **Duferco**, **Essar**, **Hadeed** (part of SABIC), **HKM**, **Isdemir**, **POSCO**, **Rautaruukki**, **Sail**, **Salzgitter**, **Tata Steel**, **Tenaris**, **Ternium**, **Třinecké železářny**, **Usiminas**, **US Steel**, **VDEh** and **Voestalpine**. The global representation of the members with the meeting locations can be seen in Figure 4.1.



Figure 4.1 Geographic distribution of the project team and meeting locations

4.4 Pre-survey

In the beginning of the project, May 2006, a pre-survey questionnaire was sent to the member companies in order to find out what the most important water-related issues being faced by the steel industry are. 48 member companies took part in the questionnaire and the main water related issues faced by these companies in order of importance were:

⁷ Tata acquired Corus during the project

1. Quality of wastewater
2. Water recycling and minimisation of consumption
3. Pollutants in the water
4. Implementation of new water management technologies
5. Cost-effectiveness of wastewater treatment technologies
6. Quality of process water
7. Reduction in fresh water consumption
8. Wastewater treatment technologies
9. Threat of shortage in water resources in future
10. Change in approach to water strategy & policy (IISI, 2006)

The above issues were broken down to specific key performance indicators, which were then used to build up the survey for data collection. During the meetings it was decided that next to looking at water in process format and gather quantitative data, an additional part measuring quality of water management was to be developed. This water management performance matrix was used to measure softer water management issues such as level of water metering and targeting, water manager and organisation, etc. in a quantitative format scale.

4.4.1 Scope and Boundaries

The reliability of any survey always depends on the reliability of the data. Therefore in case of comparisons or benchmarking, it is necessary to take into account the quality, accuracy and origin of the data in order to avoid misinterpretation, wrong conclusions or unjustified generalisations.

In this case the working group of the worldsteel Water Management Project was well aware of the fact that it is difficult to compare the use of water between different steel plants for several reasons. These difficulties include:

- Lack of (exact) monitoring data: The participants completed the questionnaires with the existing knowledge and in many cases estimates were used and in some cases entries were left open.

- Interpretations of the survey: The survey was distributed with default value ranges. It was possible to fill in >90% of the survey in this matter. For less predictable entries in e.g. (sub) processes, no default ranges were provided. These data are especially hard to use for comparison between different steel plants.
- Mistakes in submitting data: It is likely that in some cases questions were misinterpreted. By carefully scrutinising all answers and asking participants to reassess, a huge step in improving quality was achieved. It is however possible that the report still contains some misinterpretation and inaccuracies.
- The process configuration of steel companies varies a lot: Only data from comparable configurations can be compared. In some cases the main processes concerning the water use are interlinked.
- Completing information: The level of detail given varies a lot between participants. Sometimes only totals could be provided without the requested differentiations. Some participants had difficulty completing the data for reuse flows. Some participants included storm water, some didn't. In some cases what was filled-in is not clear and the same concerns municipal water.
- Difference in processes between steelworks: In cases of the use of treatment plants for different flows it is difficult to compare a certain flow from a certain process between different steel plants at the level of (sub) processes.

All these factors influence the results and must be taken into account when using the data.

4.4.2 Methodology

After the first attempt to collect water management data with the original web-based survey, the re-launch can be characterised by 7 different phases of:

Phase 1: Development of the (new) Water management Survey.

Phase 2: Request to all the worldsteel members to participate and to provide information.

Phase 3: Analysis and handling the data.

Phase 4: Development of water flow charts + extra data quality improvement request.

Phase 5: Request for description of good practises (case studies).

Phase 6: Analysis, handling and comparison of the final data.

Phase 7: Writing of the report.

4.4.2.1 Phase 1: Development of the (new) Water Management Survey

The first phase of the project concentrated on what kind of data are required in order to carry out benchmarking and how high-quality data could be collected in a way that would provide data that are understandable and suitable to compare. Because of the fact that the first attempt to collect data with a web-based survey failed, lessons were learned and a more user-friendly type of survey was developed. The reason for using Microsoft Excel as the base of the survey was that it's flexible, well known and used all over the World. The new survey was developed by the Environmental Management Department of Tata Steel in Ijmuiden, the Netherlands, based on the initial survey that was developed by the author of this thesis. Furthermore the water management matrix was developed solely by the author.

Water consumption, water use, water discharge etc. in the steel industry depend very much on several different factors. Therefore it is difficult to use one fixed survey format to collect data from all the different plants. The water use of a steel plant (inflows/outflows/re-use or not/applied techniques etc.) depends on several factors, including; local legislation, geographical situation, economical situation, the types of water available and (in many cases the unique) combination of processes and sub-processes.

The survey was built so that all identified processes, sub-processes, water types, inflows, re-use flows, etc. had their own entry to fill-in. Whenever possible a default range was given. But as some things cannot be predicted, especially not when it comes to water management, the survey also allowed to fill-in data outside the range, especially when no default values were predicted.

To understand and complete the survey in a correct way, a manual with examples etc. was provided as a tool, together with the survey.

The following data were asked for in the survey.

General information about the plant

- Name / address etc.
- Contact
- Annual production of crude steel
- Annual intake and discharge numbers (distinction in types of water)

Specific information about the processes

- Kind of processes (like coke making, casting etc) and annual production
- Kind of sub-processes (like once-through cooling⁸, quenching etc.)
- Water intake (flows in m³/day)
- Water variety (seawater, potable, ground-water etc.)
- Flows of water re-use (where from/where to/daily amount)
- Water discharge (destination: surface water or ext. sewage works, daily flows)

This part of the survey was especially difficult to complete. To be able to compare the numbers from different sites, some conditions had to be taken into account. The most important conditions were:

- Intake water = water from outside the plant e.g. fresh water like potable water, groundwater, seawater.
- Re-use water = process water discharged is reused in another process. This part was left open to the participants and they were allowed to qualitatively describe the outflows for re-use, origin and destination.
- Total inflow = total intake + re-use water. The total inflow is a number that can be compared very well between the same processes from different plants.
- Outflows were divided into discharge to sewage works, discharge to surface water, outflow for re-use, and outflow to other. With sewage works is meant an external sewage works. Every treatment plant inside the facility is considered not a destination but a treatment. So, water that is treated in a biological treatment plant and is discharged to surface water, is supposed to be an outflow to surface water and the (biological) treatment is supposed to be considered as the post treatment technique.
- “Outflow to other” is for all other destinations.

⁸ In once-through cooling the water is discharged after use, whereas in recirculating cooling, the water lost during cooling needs is topped up by using make-up water

Techniques applied

This part of the questionnaire deals with all water treatment techniques applied. A clear distinction is made between:

- Water pre-treatment techniques
- Water post-treatment techniques

Water quality

This part of the questionnaire deals with the permit values of the effluents (concentrations of the most common compounds) in the effluents of different (sub) processes.

Water Management Matrix

The purpose of this part of the questionnaire was to find out about the qualitative water management issues within the steelworks and report them in a quantitative way to enable comparison between different steelworks. The matrix was as a self-assessment tool, rating perceived water management efforts within the company on a 5 -step scale, ranging from 0 to 4. Score of 0 reflects no interest on the specific topic in question, where as score of 4 reflects maximum interest. The topics rated were:

- Water Management & organisation
- Water Policy
- Water Metering
- Water Analyses
- Future investment plans
- Procurement
- Strategic planning
- Maintenance
- Reporting

The Water Management Matrix was developed by the author and the development began by using a utility matrix as a base that the author had previously developed in co-operation with a senior lecturer of the University of Glamorgan. Several versions of the Matrix were developed during the Water Management Project and feedback from other water professionals was used to improve it prior to this final version.

Feedback

For continuous improvement reasons at various stages of the survey the participants were asked to provide feedback on the survey. Further explanations about their survey were done on an interactive basis.

4.4.2.2 Phase 2: Request to all the worldsteel Members to Participate and Complete in the Survey

The second survey was launched and sent to all the members of the worldsteel in July 2009. In spite of the fact that this was already a second attempt it soon became clear that there was serious interest in the subject but that the timing for the re-launch was bad because of the holiday period. Therefore the deadline was extended several times. In the end, data was received from 29 participants, ranging from steelworks with only a hot rolling mill to fully integrated steel plants. Steelworks from several countries and regions took part in the survey, including: ArcelorMittal, Baosteel, BlueScope Steel, China Steel Corporation, CMC, Corus⁹, Duferco, Essar, Hadeed (part of SABIC), HKM, Isdemir, POSCO, Rautaruukki, Sail, Salzgitter, Tata Steel, Tenaris, Ternium, Třinecké železářny, Usiminas, US Steel, VDEh and Voestalpine. The participants were asked to provide data from the last 'full' production year. For some steelworks this was 2008, but due to the downturn, some of the data provided as a part of the survey dates back to year 2007.

4.4.2.3 Phase 3: Analysing and Handling the Data

Different models were developed to analyse and handle the data and make it comparable. As was anticipated, during the process of handling the data, it became clear that it is very difficult to compare steel plants when those plants don't have the same configuration. It also became clear that it is much more important to see the differences in water management on the level of main processes like coke making, casting or hot rolling instead of the level of the water management of the entire plant. From that moment the working group decided to focus on the main-processes and underlying sub processes. To compare the data, the data were calculated as the usage of

⁹ Tata acquired Corus during the project

water in m³/tonne product for each process. Based on the inflows and outflows the loss was automatically calculated. All the surveys were carefully manually checked. Unfortunately in a lot of cases, many questions and uncertainties about data remained. Therefore the project group decided to add an extra quality improvement step (Phase 4).

4.4.2.4 Phase 4: Development of the Water Flow Charts + Extra Quality Improvement Step

For each participant a water flow chart was built. The objective was to show the participants their completed survey in one picture. Mistakes and misinterpretations in this way could easily be identified.

All the participants received their own water flow chart together with additional specific questions. As an example the flow chart of the water management system from an integrated steel plant was also distributed. In reply to this information about 80% of the participants corrected their data. This phase was a crucial step to improve the quality of the received data.

4.4.2.5 Phase 5: Request for Description of Good Practices

Initially the objective of the water management working group was to identify the best practice for water-usage in the steel industry. Because of reasons mentioned before, this objective soon became far too ambitious. Too many things differ from site to site like the already mentioned legislation, geographical situation, economical situation, and especially the availability and quality of the water. In many cases, the unique combination of sub-processes makes comparison even harder. In the received surveys it was very hard to find two comparable configurations. Based on this observation the working group decided to look for good practices instead. Based on the received information good practices were identified and participants were asked to describe those practices in detail.

4.4.2.6 Phase 6: Analysing, Handling and Comparing the Final Data

The following information was extracted from the data:

1. For each steel plant the water-usage was calculated in m^3/tonne of product for each process.
2. Comparison of steel plant configuration, total production and total water-usage was made.
3. Comparison of data at the level of the water consumption of the main processes (All results are expressed in m^3/tonne of specific product. As an example, water usage in coke making is expressed in m^3/tonne of coke and the blast furnace water usage as m^3/tonne of pig iron).
4. A software selection tool was developed to select pre treatment techniques (on the level of (sub) processes/kind of water/applied techniques etc.
5. A software selection tool was developed to select post treatment techniques (on the level of (sub) processes/kind of water/applied techniques etc.
6. A software selection tool was developed to select water quality (on the level of sub-processes.
7. Comparison of the water management efforts of the participants was made.
8. Finalised and updated water flow charts of all the participating steel plant were put together.
9. A database with all the presented and derived data was set up.

4.4.2.7 Phase 7: Writing of the Report

The writing of the report was carried out over a year as a co-operation between the water management project members and the worldsteel. The report was published in May 2011.

4.5 Results

These results outline differences in water quantity and quality performance in the 29 steelworks that took part in the survey. Port Talbot Steelworks' results are listed as number 24 within the results.

4.5.1 Survey Data

The 29 steelworks that completed the survey represent around 8% or 110.9 million tonnes of the World's annual steel output. The number of different facilities within the participating steelworks together with combined production figures for the different facilities can be seen in Figure 4.2. All together 17 integrated steel plants took part in the survey as indicated by coke making, sintering, blast furnace and basic oxygen facility numbers.

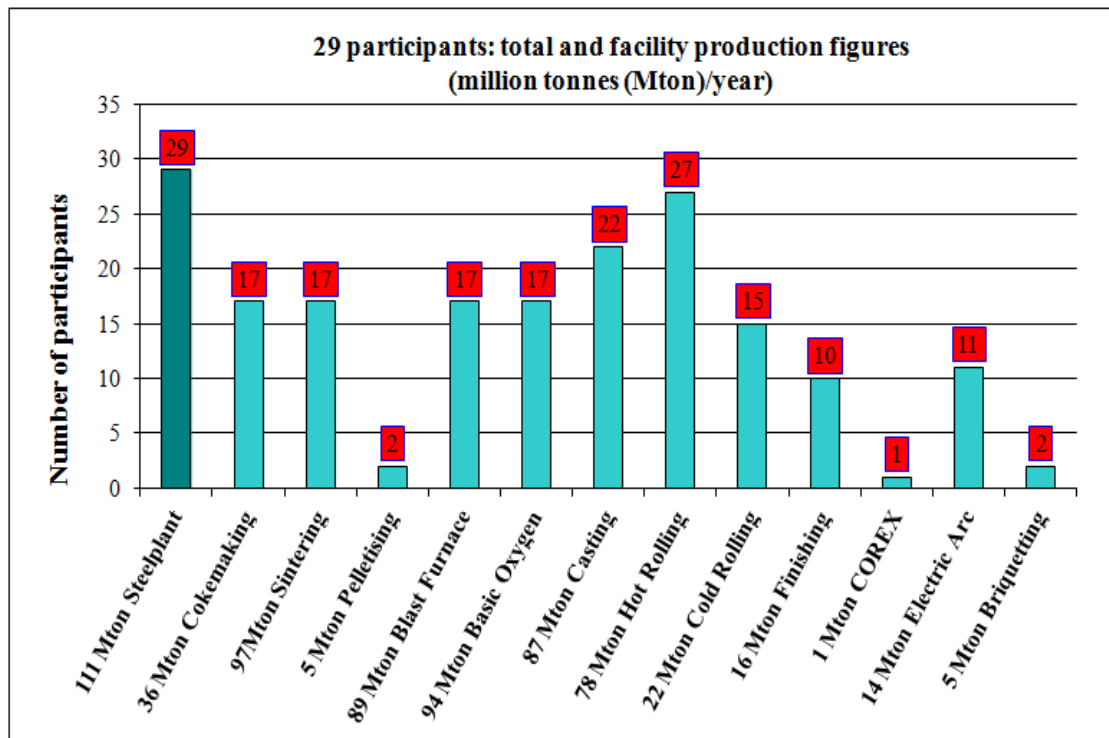


Figure 4.2 Number of different facilities within the participating steelworks (Suvio et al., 2010a)

As seen in Table 4.2, the highest integrated individual production figure was 14.9 million tonnes per annum and lowest 2.5 million tonnes per annum. Out of the 12 non-integrated steel plants, 8 steel plants use an electric arc furnace (EAF). Out all the 29 steel plants, 2 use both, the basic oxygen and electric arc furnace. Out of the non-integrated steel plants, the highest individual production figure was 4.6 million tonnes per annum and lowest 0.1 million tonnes per annum. The average overall production figure for the participating steel plants was 3.8 million tonnes per annum.

Table 4.2 Data from worldsteel water survey (Suvio, et al., 2010a)

WORLD STEEL WATER SURVEY																															
Overview processes																															
Plant number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29		
million tonne product / year																															
production million ts/year	5.3	10.2	6.9	0.5	0.3	2.0	4.3	4.6	2.5	5.4	0.8	1.2	0.9	6.3	0.7	0.8	0.1	0.9	4.2	2.8	5.6	6.4	14.9	4.3	2.6	5.5	3.2	4.3	3.3		
Cokemaking	2.3	4.2	2.2				1.5		0.7	1.4				3.2					1.3	2.3	2.3	1.4	7.3	1.0	0.9	1.1	1.8	1.3			
Sintering	5.2	13.1	4.4				2.6		2.5	2.7					6.5					5.9	2.4	6.5	8.2	16.3	3.9	2.7	4.7	4.1	5.4		
Pelletising		0.1	4.6					0.0																							
Blast Furnace	5.1	9.7	6.1					4.0		2.0	4.6				6.6					3.7	2.8	6.3	6.3	13.9	3.9	2.4	4.8	3.1	3.7		
Basic Oxygen	5.5	10.4	6.9					4.3		2.4	5.4				6.3					4.2	2.9	5.8	6.3	14.1	4.4	2.6	5.5	3.3	3.9		
Casting	5.3	10.1	6.8			0.7	4.3	4.6	2.4		0.8	1.2		6.1	0.7	0.5		0.9	4.1	2.9	5.6		13.4	4.3	2.6		3.1	3.8	3.3		
Hot Rolling	3.5	6.9	4.8	0.5		2.1	3.2	4.7	1.7	5.1	0.7	1.0	0.7	2.5	0.5	0.4	0.1	0.8	4.5	0.6	4.6	4.3	12.6	3.1	2.3		0.6	2.8	3.1		
Cold Rolling	0.1	2.7	2.8		0.3	1.1	1.5	1.2		2.7									3.0		1.4		3.3	1.1					0.8		
Finishing			0.9		0.2		1.4	0.3		1.0	0.7	0.9		4.6							5.4		0.0	0.7							
COREX												0.9											0.0								
Electric Arc						0.8		4.6	0.03		0.8	1.2	0.9		0.7			0.9					0.94						3.31		
Briquetting																						1.0							3.8		
Total intake water m ³ /ts	30.8	6.5	31.0	33.1	0.8	3.7	5.1	70.3	2.3	115.4	5.3	43.4	5.4	69.2	1.5	0.0	1.0	1.1	4.7	148.0	6.8	14.8	7.3	33.8	17.5	7.3	80.4	2.7	2.6		
Total discharge water m ³ /ts	28.8	1.5	28.5	31.4	0.6	2.4	2.6	69.5	1.8	110.5	2.6	41.8	0.0	66.1	0.8	49.3	0.0	0.3	2.8	144.6	2.6	12.9	3.5	28.8	14.8	6.1	77.0	0.0	0.6		

As can be seen in Table 4.2, consumption¹⁰ and discharge performance figures are based on m³/tonne of crude steel (m³/ts). However, this concept often refers to steel produced via the basic oxygen plant route or electric arc furnace route. In some cases however, due to the lack of the above production facilities, consumption is expressed as the next possible production unit, e.g. as a tonne of rolled product. With individual facilities, the water related figures are always outlined as a tonne of product of the facility in question.

4.5.2 Calculations for Water Related Performance

In the following calculations, data from steel plant number 16 has been excluded, due to not being able to balance its flow data. Therefore the following calculations include the remaining 28 participants. Other data for plant number 16, including the water management matrix score is outlined as part of the results.

As seen in Table 4.3, the annual water intake or consumption within the 28 steel plants totals little over 3 billion m³ of water or 28.4 m³/ts. The annual water inflow to the facilities of the different steel plants averages 29.7 m³/ts. The remaining 1.3 m³/ts difference is achieved by water reuse, which creates a 4.4% portion of the total water intake.

Table 4.3 Calculations for water related performance

Calculations for 28 steel plants		
Annual steel production 110.1 million tonnes		
Annual water intake	3,129,063,984m³	28.4m³/ts
Annual water reuse	143,920,058m³	1.3m³/ts
Annual water inflow	3,272,984,042m³	29.7m³/ts
Annual once-through cooling	2,560,847,489m³	23.2m³/ts
Annual total discharge	2,801,462,260m³	25.4m³/ts
Annual discharge surface water	2,764,914,272m³	25.1 m³/ts
Annual discharge sewage	36,547,988m³	0.3 m³/ts
Annual water loss	297,349,055m³	3.0m³/ts

¹⁰ Consumption within this chapter refers to: intake water, when a complete steelworks is in question and actual water needed by the process or facility (intake + reuse water) when talking at process level.

Out of the 28.4 m³/ts of water consumed by the steelworks, 25.4 m³/ts is discharged, leaving a loss of 3.0 m³/ts or a total of just under 300 million m³, which is a 10.5% fraction of all the water consumed. Out of the total 25.4 m³/ts of discharge, a large portion of 25.1 m³/ts is discharged to surface waters and the remaining 0.3 m³/ts is discharged via sewerage networks.

4.5.3 Steel Plants' Water Consumption and Discharge

As seen in Figure 4.3, water use and discharge varies greatly between different steelworks. Consumption ranges from under 1 to near 150 m³/ts with a standard deviation of 36.9 m³/ts, therefore indicating a great spread in the data.

When analysing the survey results, a distinction can be made between two different steel production routes. The first one is the basic oxygen steel making (BOS) route or the integrated steel making route and the other electric arc furnace (EAF) route. Out of the total 110.1 million tonnes of steel produced by the 28 steel plants that participated in the survey, the 17 integrated steel plants that took part produced 94.8 tonnes or 5.6 million tonnes on average per annum, whereas the non-integrated plants produced a total 15.3 million tonnes per annum or an average 1.4 million tonnes per annum.

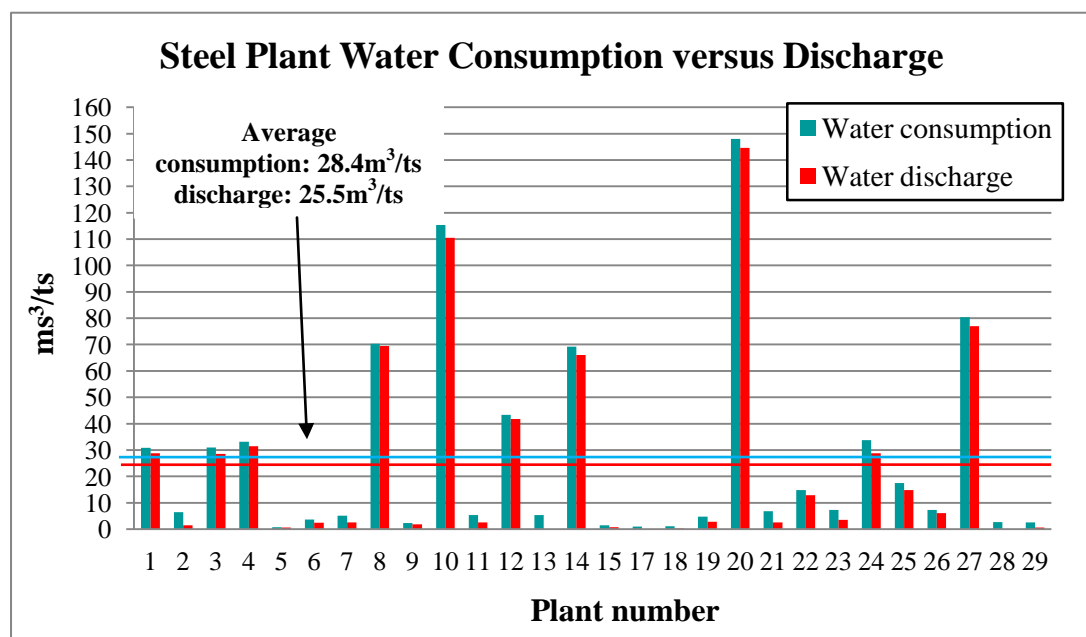


Figure 4.3 Steel Plant water consumption and discharge figures

Only 10 steel plants out of 28 consume and discharge more than the average amount of water per tonne of steel (m^3/ts) (Figure 4.3). Out of these, 4 are actually close to the average water consumption and discharge line. 15 steel plants consume and discharge well under $10 \text{ m}^3/\text{ts}$, out of which 9 steel plants consume and discharge very little, under $5 \text{ m}^3/\text{ts}$.

Especially with the steel plants with higher consumption and discharge figures, the water consumption and discharge figures are very close to each other as can be seen in Figure 4.3. With the steel plants that are consuming much less water, the water discharge figures are often considerably lower than the consumption figures. This is likely to be due to lack of water in the areas where the steel plants are located, which leads to use of closed-loops and water recycling and reuse solutions in the steel plants' processes.

4.5.4 Integrated versus Non-Integrated Steel Plants

As seen in Table 4.4, there are few distinctive differences between water performance at integrated and non-integrated steelworks. The non-integrated steel plants only reuse an average of $0.4 \text{ m}^3/\text{ts}$, whereas the integrated steel plants reuse $1.5 \text{ m}^3/\text{ts}$. Also the annual once-through cooling figures are higher for non-integrated plants at $25.8 \text{ m}^3/\text{ts}$, compared to the integrated figure of $22.8 \text{ m}^3/\text{ts}$. On the other hand the non-integrated steel plants lose less water at $1.6 \text{ m}^3/\text{ts}$, against the $2.9 \text{ m}^3/\text{ts}$ that is lost by the integrated plants. Furthermore, the non-integrated steel plants hardly discharge water to sewage, where as the same figure for the integrated plants is $0.4 \text{ m}^3/\text{ts}$.

4.5.5 Water Performance per Facility

As with individual steelworks, there are great differences between the average water consumption and discharge figures of the facilities within the steelworks (Figure 4.4). As can be seen in the Figure, the supporting functions described as 'rest' consume by far most of the water with an average figure of $24.3 \text{ m}^3/\text{tonne}$ of product, which is well beyond any of the actual facilities. The 'rest' supporting functions to steel plants' operations often include power generation, equipment and indirect cooling activities.

When looking at water consumption and discharge of the actual facilities within the steel plants, the COREX figures with 18.1 m³/tonne of product, stand out much higher than the rest, it should however be noted, that only one steel plant (number 12) with a COREX process took part in the survey. Therefore, it has not been included in the results.

Table 4.4 Water calculations for integrated and non-integrated steel plants

Calculations for 17 integrated and 10 non-integrated steel plants				
Type of plant	Integrated		Non-integrated	
Annual steel production	94.8 tonnes/annum		15.3 tonnes/annum	
Unit	m³	m³/ts	m³	m³/ts
Annual water intake	2,706,844,277	28.6	422,219,707	27.6
Annual water reuse	138,215,627	1.5	5,704,431	0.4
Annual water inflow	2,845,059,903	30.0	427,924,139	28.0
Annual once-through cooling	2,165,353,929	22.8	395,493,560	25.8
Annual total discharge	2,403,153,856	25.3	398,308,404	26.0
Annual discharge surface water	2,366,763,913	25.0	398,150,359	26.0
Annual discharge sewage	36,389,943	0.4	158,045	0.0
Annual water loss	272,391,924	2.9	24,957,131	1.6

Of the remaining production facilities, a good assessment of where most water is being consumed, discharged and lost can be carried out. As seen in Figure 4.4, most of the major steel plants' production facilities consume between 3 and 5 m³/tonne of product. As expected, the Blast Furnace has the highest figure at 5.7 m³/tonne of product, followed by Hot Rolling with 5.0 m³/tonne of product, Cold Rolling with 4.6 m³/tonne of product and Cokemaking with 4.5 m³/tonne of product. The discharge figures for these same facilities are 4.8 m³/tonne of product for Blast Furnace, 4 m³/tonne of product for Hot Rolling, 3.5 m³/tonne of product for Cold Rolling and 3.4 m³/tonne of product for the Cokemaking. The smaller water users include Basic Oxygen Steelmaking, Sintering, Pelletising and Briquetting as can be seen in Figure 4.4.

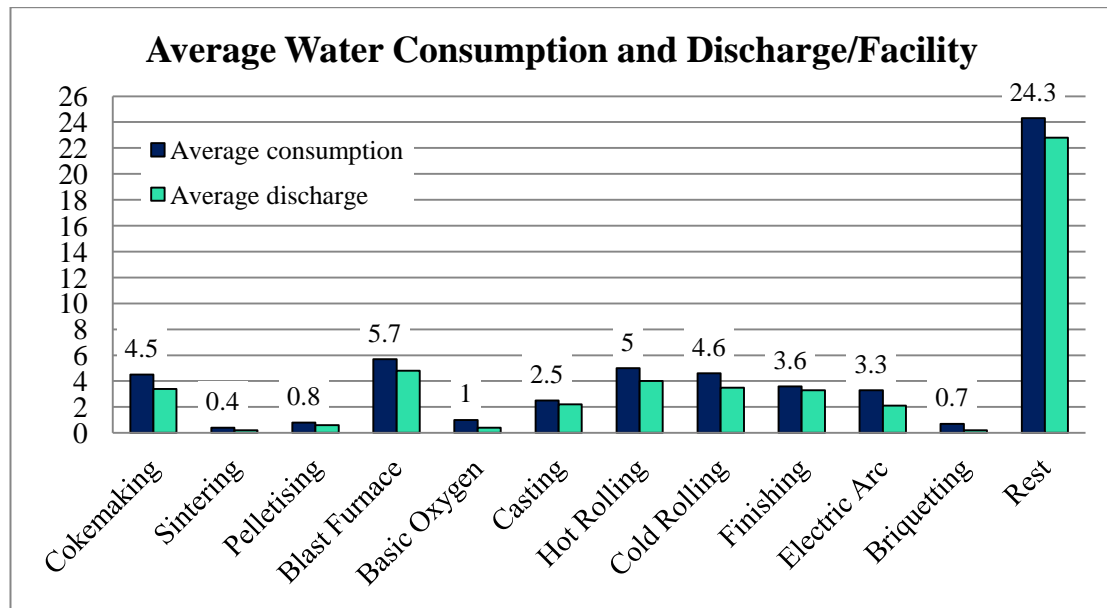


Figure 4.4 Steel plants water consumption and discharge figures for facilities

4.5.6 Coke Making

When looking deeper into some of the individual facilities, it can be seen that in some cases few individual plants have much higher consumption figures than the others. This is the case for example with the cokemaking plants, where the three most consuming plants rate as follows:

1. 37.1 m³/tonne of coke (plant number 7)
2. 16.0 m³/tonne of coke (plant number 8)
3. 4.5 m³/tonne of coke (plant number 19)

As mentioned before, the average water consumption figure for the 17 cokemaking plants that took part in the survey is 4.5 m³/tonne of coke, if however, the highest value is dropped out, the consumption drops down to 2.5 m³/tonne of coke and if two of the most consuming plants are left out and an average calculated for the 15 remaining plants, the figure drops down to mere 1.6 m³/tonne of coke. Taken that the two highest consumption figures are multiple times higher than any of the rest, it appears that this last figure is rather more correct as an average consumption for coke making than the original 4.5 m³/tonne of coke, which would make the coke making a minor consumer of water in relation to most of the other facilities within the steelworks.

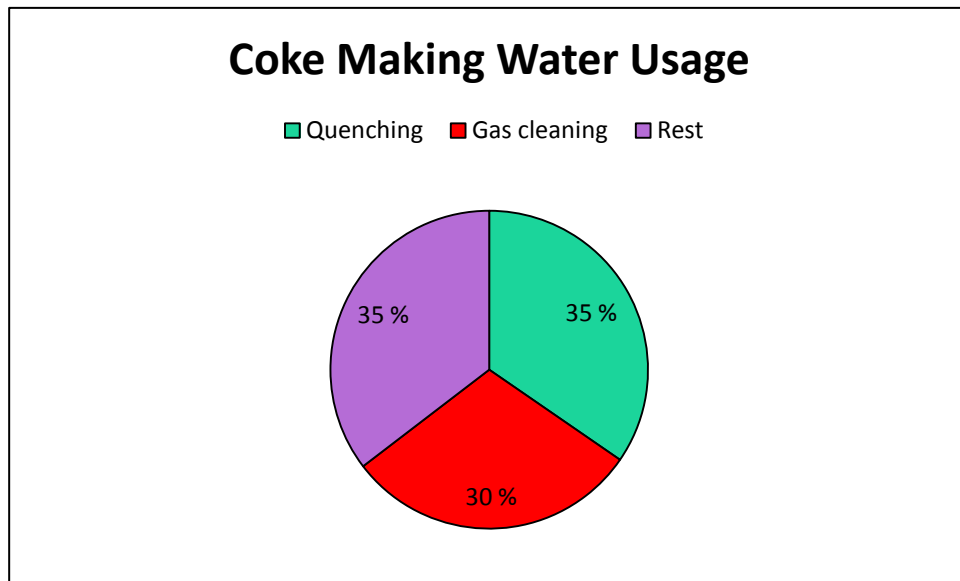


Figure 4.5 Coke making water usage breakdown

As outlined in Chapter 3, water does however have a very important function in coke making and is used for two very important functions, namely gas cleaning and quenching. As seen in Figure 4.5, out of the total water used in coke making, an average 35% of the consumed water is used for quenching, where as the same figure for gas cleaning is 30%, the rest is used for cooling, etc.

When comparing the water usage between the different processes in coke making and as follows within the blast furnace operations, only plants that listed separate consumption figures for all the main processes within the facilities have been included in the calculations. However, these total in both cases ten or more steel plants.

4.5.7 Blast Furnaces

Although not with as clear a margin as with the coke making plants, the blast furnaces have a few bigger consumers, with the biggest consumption figures as follows:

1. 28.2 m³/tonne of iron (plant number 3)
2. 22.1 m³/tonne of iron (plant number 10)
3. 7.1 m³/tonne of iron (plant number 26)

When normalising the average blast furnace water consumption figures without the biggest consumer, a consumption figure of 4.3 m³/tonne of iron is achieved, the same figure without the two biggest consumer is 3.1 m³/tonne of iron. Due to the nature of the blast furnace operation, large volumes of water are used for cooling, the blast furnace hearth cooling being the biggest consumer. As seen in Figure 4.6, 62% of the water inflow to the blast furnaces is used for once-through cooling. Only 12% of the water is used by circulating cooling. As with coke making, blast furnace gas cleaning requires large volumes of water and as seen in Figure 4.6, 21% of all the water consumed at the blast furnace is used for this purpose.

As with coke making and blast furnace, similar comparisons could be carried out for Basic Oxygen Furnace process looking at water consumption in gas cleaning and cooling duties, as well for Hot Rolling and Cold Rolling, looking at how the once-through and circulating (closed-loop) water usage has been divided. Coke Making and Blast Furnace operations were nevertheless chosen here as they are the facilities with most varying water consumption and biggest environmental factors, including crucial gas cleaning requirements.

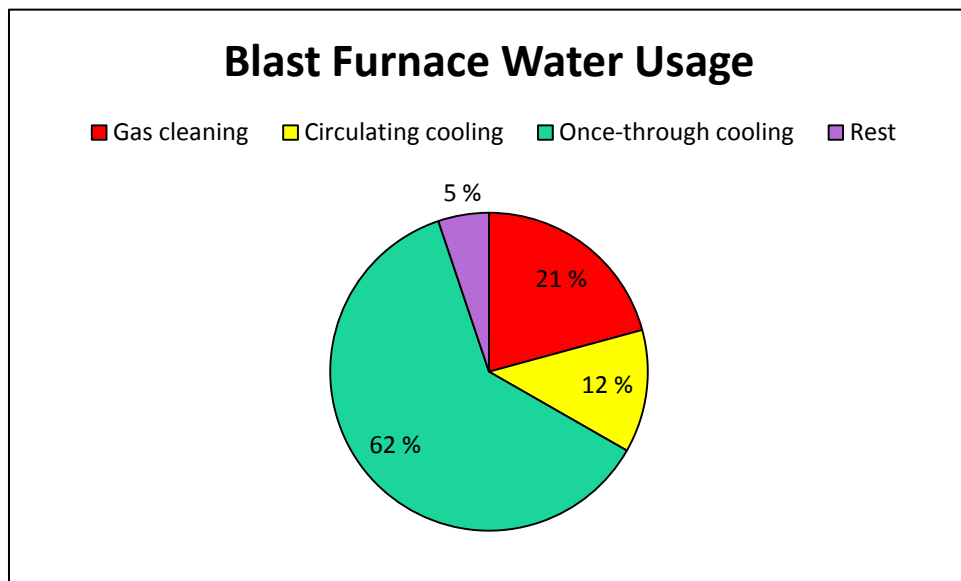


Figure 4.6 Blast furnaces water usage breakdown

4.5.8 Cooling Water Usage

Overall, it should be noted that the water consumption and discharge varies hugely depending on the plant, configuration, geographic situation (availability of water) and

local legislation. Large volumes of water are consumed by once-through cooling especially at locations near the seaside (Figure 4.7), while especially when water is scarce, closed-loops and circulated cooling plays an important part and minimum amount of water is consumed or used as a make-up water.

As outlined by Figure 4.7, one can distinguish that large integrated steel plants are using by far most of their water for cooling purposes and most of this cooling is done with once-through cooling systems. Most of the water used for the once-through cooling, next to sea water, is other non-potable water, which in most cases is fresh water from rivers and reservoirs. Out of the 10 biggest once-through cooling users,, 5 are using sea water for their cooling, 3 other non-potable and 1 is using brackish water. Other non-potable water is mostly used for non-once-through cooling activities.

As mentioned before, out of the total water consumed at the steel plants, on average 82% of water is used for once-through cooling. It should be noted however that these figures are different for BOS and EAF routes at 80% and 93% respectively.

Large portions of the water used for once-through cooling is used for cooling purposes at the supporting functions, including cooling for power generation. Figure 4.4 outlines the water-related performance of the supporting functions as ‘rest’ in relation to the other facilities within steelworks.

4.5.9 Water Management Matrix

As a part of the water management survey, the participants were requested to fill-in a water management matrix (Table 4.5) as a form of self-assessment. The matrix was developed by the author of this thesis and its purpose was to provide results that give an understanding of the importance of the water management activities within the organisation, next to the hard data gathered using the survey. As can be seen in Table 4.5, the participants were asked to rate 9 different topics on a scale of 0 to 4, where score zero is equating to very low level of water management activities on the specific area and four equating to a high level of water management activities.

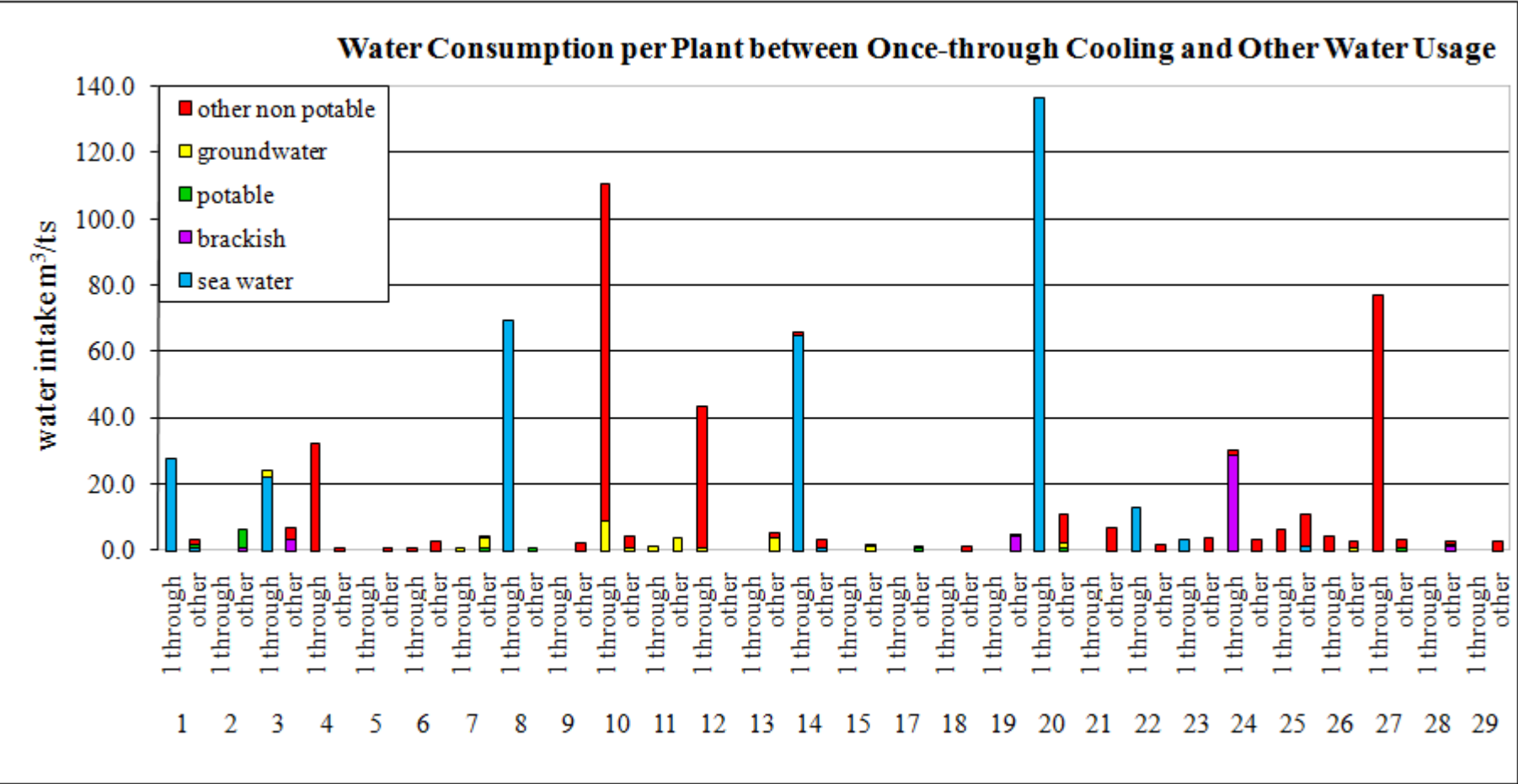


Figure 4.7 Water consumption per plant between once-through and other water usage

Table 4.5 Water management matrix

	0	1	2	3	4
Water Manager & Organisation	Unclear responsibilities	Part-time water manager with limited authority or influence	Clear responsibilities with part-time water manager	Dedicated, full-time water manager with influence and power	Full-time water manager and high-powered water committee
Water policy	No policy	An unwritten set of guidelines	Policy references in environmental or other policies	Formal water policy, but no active review process	Formal water policy, regular reviews and commitment of top management
Water Metering	Billing meters	Billing meters with limited sub-metering (e.g. potable water meters only)	Substantial metering and sub-metering	Substantial metering and sub-metering, water metering reporting party/division	Extensive metering on all the facilities, water metering data reported
Water Analysis	Meters checked against utility bills	Some analysis reference to	Water performance reports issued internally	Water performance compared against historical data and benchmarking	Advance automated monitoring and targeting with alarming & trend analysis
Future Investment Plans	Nil	Anything with quick payback	Capital spending on replacements only	Some planned investments to reduce water consumption and/or improve water efficiency	Major planned investment(s) to reduce water consumption and/or improve water efficiency
Procurement	Water efficiency not considered when purchasing new plant/equipment	Water efficiency occasionally taken into consideration in new purchases	Water efficiency considered on utility plant only e.g. water treatment plant, etc.	Procurement policy provides clear guidance on water consumption for new purchases	Procurement policy including water and environmental performance
Strategic Planning	Water management planning is short-terms only	Strategic planning for water management is long-terms but isolated from the other planning processes	Water management only loosely associated with overall strategic planning	Water management function is clearly established but not fully integrated into strategic planning	Full strategic plan for water in place with times scales and resources agreed and allocated
Maintenance	No maintenance plan, leaks fixed when and if resources become available	Periodic maintenance inspections, leaks are given low priority	Maintenance plan exists, some preventative maintenance carried out, leaks are given moderate priority	Comprehensive preventative maintenance and inspection plan, leaks are given high priority	Comprehensive preventative maintenance and inspection plan, leaks receive special priority and resources
Reporting	No periodic reporting of water statistics to senior technical or operations management	Annual reporting of water issues to senior technical or operations management, e.g. Manager Steelmaking	Monthly reporting of water issues to senior technical or operations management, e.g. Manager Steelmaking	Weekly reporting of water issues to senior technical or operations management, e.g. Manager Steelmaking	Daily reporting of water issues to senior technical or operations management, e.g. Manager Steelmaking

Table 4.6 Water management matrix results (Suvio et al., 2010a)

Plant #	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	Average
Water Manager & Organisation	3	3	3	1	2	1	4	4	3	3	2	3	3	3	2	2	3	2	1	3	2	3	4	3	2	4	2	3	2	2.6
Water Policy	3	4	3	1	2	1	3	3	2	4	2	2	2	4	1	4	4	2	3	2	2	3	4	1	2	4	2	4	4	2.7
Water Metering	3	3	4	0	3	0	4	2	3	4	3	2	3	4	2	2	2	2	3	4	1	2	4	2	2	3	3	0	4	2.6
Water Analysis	3	3	4	1	2	1	4	1	3	4	3	2	2	4	4	3	3	3	4	2	1	3	4	2	2	3	3	4	3	2.8
Future Investment Plans	3	4	2	3	0	4	2	4	3	3	3	3	3	4	4	2	2	3	0	3	3	3	4	4	4	3	0	3	4	2.9
Procurement	3	3	2	2	3	1	2	4	4	3	3	4	3	4	1	2	3	0	2	3	2	4	3	1	2	2	2	3	2	2.5
Strategic Planning	4	4	3	2	2	2	2	3	4	4	3	3	3	4	3	2	3	4	1	0	2	3	4	2	1	3	0	3	3	2.7
Maintenance	4	4	2	2	3	1	2	4	2	3	3	4	3	3	4	3	3	3	2	2	4	4	3	2	2	3	2	2	4	2.9
Reporting	4	4	3	0	2	0	4	1	3	4	2	2	2	4	2	3	3	3	1	2	2	3	4	1	2	3	2	2	4	2.4
Score out of 100%	81%	89%	72%	33%	53%	31%	75%	72%	75%	89%	67%	69%	67%	94%	64%	64%	72%	61%	47%	58%	53%	78%	94%	50%	53%	78%	44%	67%	83%	67%

As can be seen in Table 4.6, the average scores for the nine different water management areas vary from 2.4 to 2.9. On average the participants rated their efforts in Maintenance and Future Investment Plans the highest, with an average score of 2.9, whereas the lowest average score was in Reporting with 2.4 followed by Procurement with a score of 2.5. As can be seen in Table 4.6, some steel plants assessed themselves to score in all areas at 3 or 4 out of 4, giving them a fully green line and an average percentage score around 80-90% out of the full 100%. These plants include numbers 1, 2, 10, 14 and 23.

On the other hand, there are a few plants that scored all but one of the nine different water management areas at 0-2 and have an average percentage score around 30-50% (Table 4.6). These plants include numbers 4, 6 and 25. The average score for all the 29 plants is 2.7 or 68%.

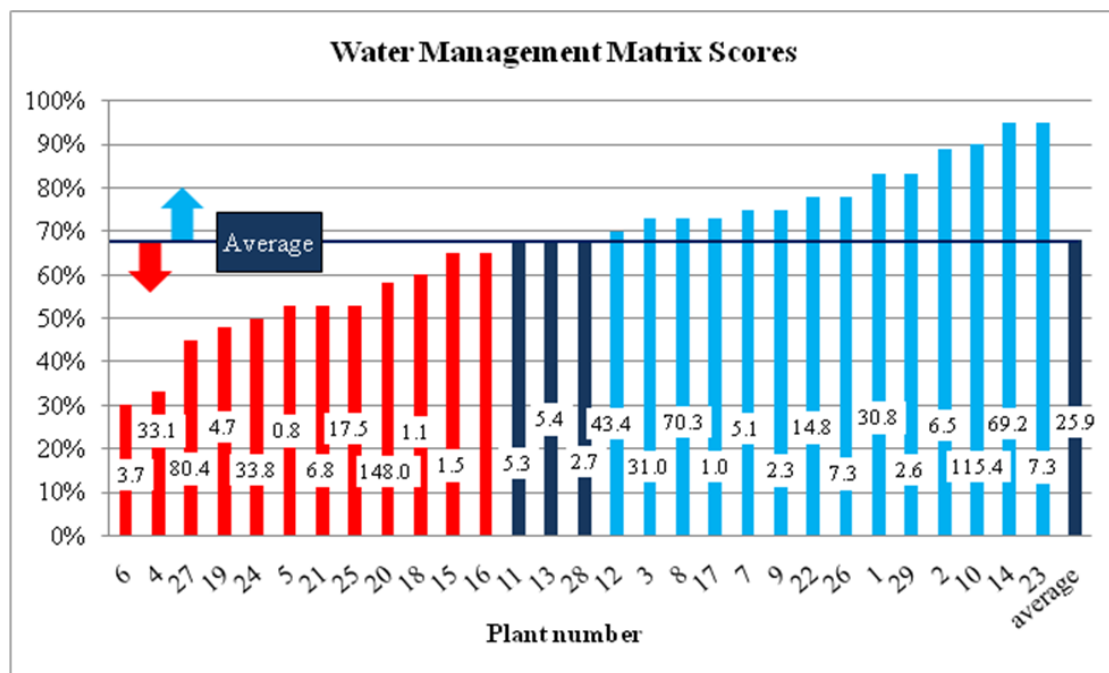


Figure 4.8 Water management matrix results¹¹

As can be seen in Figure 4.8, there is a wide range of difference between the scores of different steel plants, with plant number 6, scoring themselves lowest at only 31% and plant number 23 scoring themselves highest at 94%. The water management matrix was built so that the expected average score would be around 50%, what is striking

¹¹ The production figures of the specific facility are visible within the bars in million tonnes/annum

however is that the participants rated their water management efforts rather high and averaged a score of 68%.

Out of the 17 integrated plants, only 6 are in red in Figure 4.8, namely plant numbers 19, 20, 21, 24, 25 and 27. Out of the 11 non-integrated plants, 6 are in red, which would indicate that overall, water is deemed to be somewhat less important at integrated than at the non-integrated steel plants but this might merely reflect the fact that much less water is consumed in non-integrated steelworks. As can be seen in the Figure, there is no link between the water consumption per tonne of steel and the actual steel production tonnages, as there are low and high steel producers in both ends of the graph.

In order to expand on the water management matrix results, the Water Management Working Group members were asked to give multipliers on a scale of 0 to 4 to the nine different water management topics based on how important they thought that the specific topic was for the overall water management within steel industry. As seen in Table 4.7, when averaging the multiplier assessment results, it can be seen that the working group members thought that the Water Management and Organisation was by far the most important topic within the matrix and therefore the most important topic for the water management within steelworks. Water Metering, Analysis and Maintenance was also rated fairly high, where as especially Procurement and Future Investment Plans were not considered that important for overall water management at steelworks.

Table 4.7 Water management matrix multipliers

Water Performance Matrix Multipliers	
Topic	Average assessment
Water Manager & Organisation	4.0
Water Policy	2.0
Water Metering	2.8
Water Analysis	2.5
Future Investment Plans	1.5
Procurement	1.5
Strategic Planning	2.0
Maintenance	2.5
Reporting	1.8

Water management scores were further re-analysed using the multipliers as a help to give them more meaning and the results of the re-analysis can be seen in Figure 4.9. As can be seen in the figure, the average results rose to 71%, while the overall variation of the results got smaller, the lowest results being 42% for plant number 6 and 97% for plant number 23. Overall the order of the different steel plants did not change a lot, apart from few exceptions, including plant number 1, whose score dropped from 81% to 65.8%. This drop indicates that the Water Management Matrix areas that were deemed important by the Water Management Working Group, were assessed lower than the other areas by the steel plant number 1.

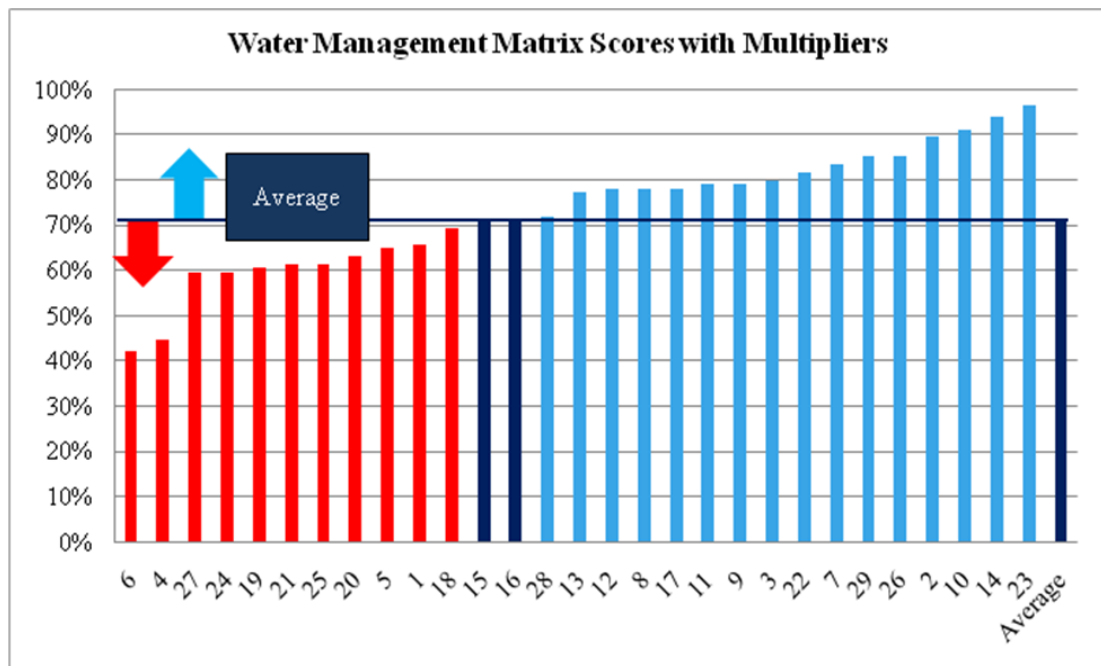


Figure 4.9 Water management matrix results with multipliers

4.6 Conclusion

Water Management Working Group ran from June 2007 until May 2011 during which a successful water benchmarking survey was compiled, data received and results analysed.

29 steel plants, including 17 integrated and 12 non-integrated, completed the survey, representing around 8% or 110.9 million tonnes of the World's annual steel output.

It was found that most of the water consumed during steel making is used for supporting functions such as cooling for power generation.

Water has an important function in iron making for environmental purposes, with coke making, for example, using 30% of all of its water for gas cleaning purposes.

Out of the main production facilities the Blast Furnace is one of the highest overall consumers and uses 62% of the consumed water for once-through cooling.

Most of the integrated steel plants use large volumes of water for once-through cooling, rather than using closed-loop water cooling systems.

Rolling activities consume and lose great amounts of water via direct water cooling.

Most of the steelworks rate their water management activities high, despite of their water related performance (m^3/ts) figures.

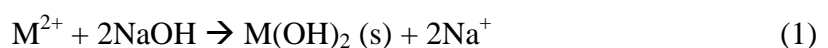
5 METAL REMOVAL FROM WASTEWATER BY CHEMICAL PRECIPITATION

5.1 Introduction

There are a number of technologies available for the removal of metals from wastewater but Eckenfelder (2000) states the most commonly employed for most of the metals is conventional precipitation by an addition of, as an example, hydroxide OH^- , sulfide S^{2-} or carbonate CO_3^{2-} , with hydroxide being the most common option. The most common hydroxide precipitating agents are (US Army Corps of Engineers, 2001):

- Calcium Hydroxide (Hydrated Lime) - $\text{Ca}(\text{OH})_2$,
- Sodium Hydroxide - NaOH and
- Magnesium Hydroxide - $\text{Mg}(\text{OH})_2$.

As is often the case, when metals enter the treatment process, they are in a stable, dissolved form and are unable to form suspended solids. The goal of metal-containing effluent treatment, by hydroxide addition as an example, is to adjust the pH via raising the hydroxide ion concentration of the water so that the metals form insoluble precipitates. Once the metals are in solid or insoluble form, they can be easily removed, leaving the water with low metal concentrations. Metal precipitation is primarily dependent upon two factors: the concentration of the metal and the pH of the water. According to Ayres et al., (1994) metals are usually present in effluent water in dilute quantities (1 - 100mg/L) and at neutral or acidic pH values (<7.0). Both of these factors are disadvantageous for metals removal. However, when hydroxide ions are added to water, it becomes alkaline, and the dissolved metals present in the water can form metal hydroxide solids, as outlined by the following hydroxide metal precipitation reaction for cationic metals in valence II:



The behaviour of metals in aqueous solution is controlled by their chemical speciation, i.e. the molecular and ionic species that they form. Metal cations (M^{Z+}) will hydrolyse to form complexes with the hydroxide ion as a function of pH and the forming complexes can be cations, neutral molecules, as well as anions. The different complexes formed are mainly governed by the valence of the metal ($Z+$) and metal ion concentration in the solution (Dyer et al., 1998).

Large volumes of water are utilised during the operation of complex integrated steelworks, which results in discharge of effluents containing low concentrations of metals in solution. As described in Chapter 3, low metal-concentration effluent is generated in most of the facilities at Tata Port Talbot Steelworks and the final effluent is currently treated by a conventional alkali precipitation and flocculant sedimentation system, especially to target zinc in solution. Effluent arisen from steelworks can be effectively treated by this type of chemical precipitation, which is particularly feasible for treating large volumes of metal containing effluents due to its simplicity and low cost.

5.2 *Metal Solubility*

A condition for successful precipitation is that the metal salts formed are so insoluble that any residual concentration of dissolved metal ions is small enough to fulfill legislative requirements (Hartinger, 1994).

In chemical precipitation, metals are often precipitated as the hydroxide, through the addition of slaked lime ($CaOH_2$) or caustic soda ($NaOH$) to a pH of minimum solubility. An example of solubility products with their solubility product constants (K_{sp}) for free metal concentrations in equilibrium with hydroxides can be seen in Table 5.1.

The degree of precipitation of metal hydroxides relates directly to the hydroxide ion concentrations i.e. pH, but the minimum solubility and the pH required for achieving it varies with the metal species and the precipitation format (type of alkali reagent used) in question. According to Metcalf and Eddy (2003) it is important to remember that the

minimum solubility will also vary depending on the other constituents in the wastewater. Metal hydroxides precipitate out of solution when they reach their solubility limit, which occurs at a certain pH (Kuyucak, 1995) as seen in Figure 5.1, which outlines a solubility curve for the most common metal hydroxides and sulphides.

Table 5.1 Solubility products with their solubility product constants for free metal ion concentrations in equilibrium with hydroxides at 25°C (Adapted from Metcalf & Eddy, 2003)

Disinfectant	Half reaction	Solubility product constant (K_{sp})
Cadmium hydroxide	$\text{Cd}(\text{OH})_2 \leftrightarrow \text{Cd}^{2+} + 2\text{OH}^-$	7.2×10^{-15}
Chromium hydroxide	$\text{Cr}(\text{OH})_3 \leftrightarrow \text{Cr}^{3+} + 3\text{OH}^-$	6.3×10^{-31}
Copper hydroxide	$\text{Cu}(\text{OH})_2 \leftrightarrow \text{Cu}^{2+} + 2\text{OH}^-$	4.8×10^{-20}
Iron (II) hydroxide	$\text{Fe}(\text{OH})_2 \leftrightarrow \text{Fe}^{2+} + 2\text{OH}^-$	4.87×10^{-17}
Lead hydroxide	$\text{Pb}(\text{OH})_2 \leftrightarrow \text{Pb}^{2+} + 2\text{OH}^-$	1.43×10^{-20}
Nickel hydroxide	$\text{Ni}(\text{OH})_2 \leftrightarrow \text{Ni}^{2+} + 2\text{OH}^-$	5.48×10^{-16}
Zinc hydroxide	$\text{Zn}(\text{OH})_2 \leftrightarrow \text{Zn}^{2+} + 2\text{OH}^-$	1.2×10^{-17}

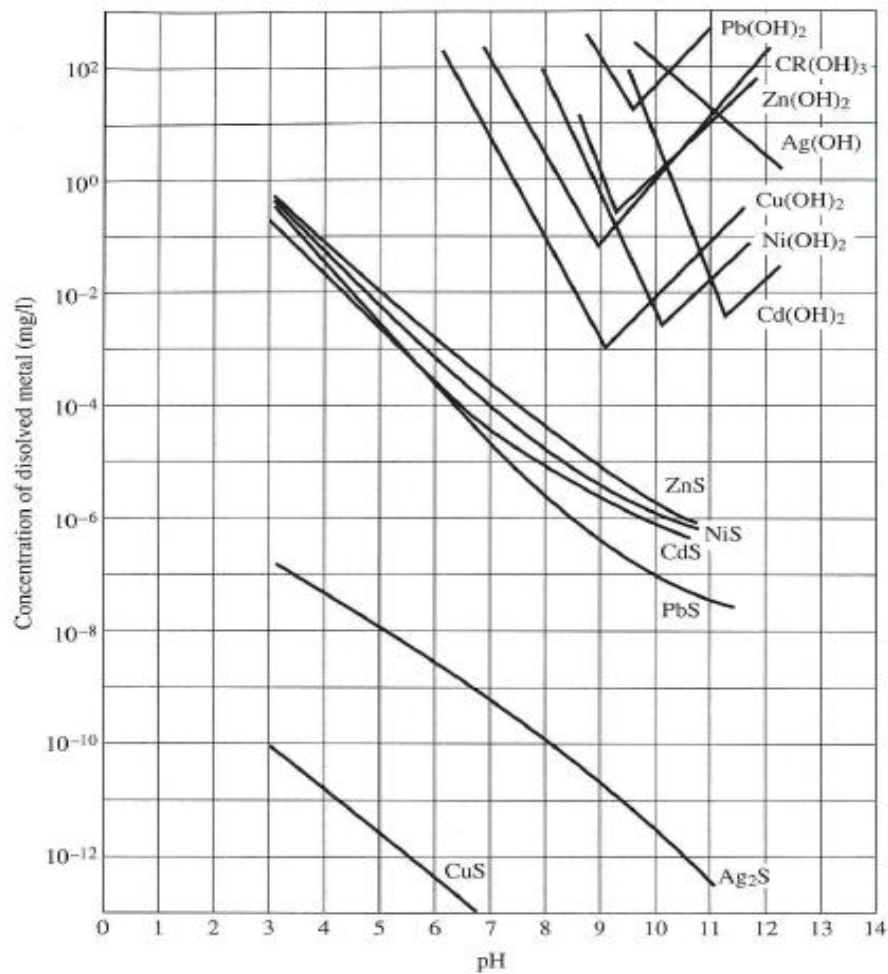


Figure 5.1 Solubility of metal hydroxides and sulphides (Eckenfelder, 2000)

Table 5.2 lists theoretical solubilities for selected metals using different chemicals with different functional elements to carry out the precipitation. As seen in the Table, metal sulphides provide lower metal concentrations than metal hydroxides with most of the main metals. Carbonate works only with some metals, but some cases, Pb^{2+} and Zn^{2+} for example, give better results in metal removal from the solution than hydroxide. The problem occurring with carbonate alkalis is that if there are high levels of acidity in the effluent, carbonate compounds can only raise the pH to 8.5 to 9.0, which is often not always sufficient for metal precipitation (Brown et al., 2002; Skousen et al., 1990). The treatment of low acid or non-acid effluent, such as steelworks final effluent can however be carried out by using carbonate reagents. If the choice is made between hydroxide and sulphite however, the latter gives better treatment efficiency as seen in Figure 5.1.

Table 5.2 Theoretical minimum solubilities achieved by using reagents with different functional element (adapted from Lanoutte, 1977; US Army Corps of Engineers, 2001 and Bullen, 2006)

Metal		Solubility of metal ion (mg/l)		
		As Hydroxide	As Sulphide	As Carbonate
Cadmium	Cd^{2+}	2.3×10^{-5}	6.7×10^{-10}	1.0×10^{-4}
Chromium	Cr^{3+}	8.4×10^{-4}	No precipitate	-
Cobalt	Co^{2+}	2.2×10^{-1}	1.0×10^{-8}	-
Copper	Cu^{2+}	2.2×10^{-2}	5.8×10^{-18}	-
Iron	Fe^{2+}	8.9×10^{-1}	3.4×10^{-5}	-
Lead	Pb^{2+}	2.1	3.8×10^{-9}	7.0×10^{-3}
Manganese	Mn^{2+}	1.2	2.1×10^{-3}	-
Mercury	Hg^{2+}	3.9×10^{-4}	9.0×10^{-20}	3.9×10^{-2}
Nickel	Ni^{2+}	6.9×10^{-3}	6.9×10^{-8}	1.9×10^{-2}
Silver	Ag^{+}	13.3	7.4×10^{-12}	2.1×10^{-1}
Tin	Sn^{2+}	1.1×10^{-4}	3.8×10^{-8}	-
Zinc	Zn^{2+}	1.1	2.3×10^{-7}	7.0×10^{-4}

Examples of the minimum metal concentration levels that can be achieved by precipitation of some metals can be seen in Table 5.3. When comparing the figures in Tables 5.2 and 5.3, it is clear that the theoretical metal concentrations are not achieved within industry. It should be noted that the minimum theoretical metal concentrations are not generally achieved when treating industrial effluents, as there are often many

different constituents present in the wastewater that might influence the treatment efficiencies.

Table 5.3 Practical effluent concentration levels achievable in metals removal by different types of precipitation (Metcalf and Eddy, 2003)

Metal	Achievable effluent concentration, mg/L	Type of precipitation and technology
Cadmium	0.05	Hydroxide precipitation at pH 10-11
	0.05	Co-precipitation with ferric hydroxide
	0.008	Sulfide precipitation
Copper	0.02-0.07	Hydroxide precipitation
	0.01-0.02	Sulfide precipitation at pH 8.5 ¹²
Nickel	0.12	Hydroxide precipitation at pH 10
Zinc	0.1	Hydroxide precipitation at pH 11

5.3 Chemical Precipitation and Co-precipitation

Several studies have been carried out looking at the process of chemical precipitation and co-precipitation and findings of the studies are well documented in the available literature (Zinck et al., 2000). Some of the most important studies are summarised here and if necessary, the reader can consult the Engineering Doctorate Dissertation of Swindley, S.P., *Control of Effluent in Steel Production*, University of Wales, Cardiff, 1999 for more references.

The behaviour of divalent metals during precipitation was described in great detail by Feitknecht, who was the first to report co-precipitation of metals from solution (1933). Using Debye-Scherrer diagrams and X-ray diffraction, he showed that basic salt precipitates consisted of hydroxides, with intercalated salt ions and were found to share a common stoicheometric composition and had similar metallic radii that enabled them to behave as isomorphs. Later, using X-ray diffraction, Feitknecht (1934) showed that a range of structures and crystal planes were formed, which were dependent on the precipitation conditions including temperature, concentration and ratio of metals. He

¹² Eckenfelder (2000) *Industrial Water Pollution Control*

proposed that when precipitates with a high density of lattice defects transform to a more ordered structure, it is possible for the cations in a lattice to be replaced with those of another metal, but also having the same valence. Schwab & Brennecke (1943) found mixed crystal of variable composition, so supporting the finding of Feitknecht on lattice defects.

Schwab & Polydoropoulos (1953) carried out co-precipitation of metal hydroxides including zinc-chromium in different ratios and concluded that at zinc to chromium ration 4:6, a plateau occurred at pH 5, corresponding to twice the quantity of hydroxide required to form chromium hydroxide. Formation of salts was also followed, concluding that formation of a basic metal salt is very much dependent on the metal in question and the type of anion and its concentration in solution. Using X-ray methods, Hartinger (1994) reported residual concentration of nickel decreasing when co-precipitated with zinc. The lowest concentrations of nickel were achieved when there was small, but equal concentrations, of both metals present in solution.

Tunay & Kabdasli (1994) investigated effects in hydroxide precipitation of complex metals, including cadmium, nickel and copper in the presence of organic complex formers using theoretical solubility comparison and NaOH laboratory experiments. High pH precipitation using lime was found to be effective when the organic ligand was effectively bound by the calcium ions, freeing the bound metals and allowing it to be precipitated.

The most extensive investigation into solubility of metal hydroxides and oxides was carried out by Dyer et al. (1998) and concluded that even though extensive data for metal solubility are available, they do not always agree on the water solubility of a particular metal hydroxide or oxide. Furthermore, the solubility of a given metal will vary significantly with pH and therefore it is insufficient to know only the solubility product (K_{sp}). Study compared existing data on solubility of metal hydroxides and oxides against solubility curves predicted by “OLI” simulation software for electrolyte chemistry. It was found that the solubility of metal in water is dependent on obvious variables including pH and temperature, but also on initial metal concentration, particle size and experimental approach. Crystallographic formation history can have a major

impact on metal solubility and depends on how long the precipitate has aged. This stable crystalline form of a solid will have a lower solubility than an active amorphous solid with sometimes a difference of more than an order of magnitude. Reliable thermodynamic “equilibrium” data may exist for only these stable crystalline solids, while the active forms of precipitates are metastable and hence never truly at equilibrium.

Swindley (1999) investigated the removal of metal complexes from solution as metal hydroxides. The work demonstrated that the solubility of metal ions and the minimum pH required for maximum precipitation varied according to the mix of the metal ions present in the solution and ratio of metals present in solution. Data showed that co-precipitation of nickel together with chromium reduces residual concentrations of both and the nickel curve can be seen to mirror the chromium curve, indicating that the two metals precipitate from solution together. Overall Swindley (1999) concludes that the combined precipitation of metal ions is advantageous for achieving lower residual metal concentration at most cases and aging of metal hydroxide precipitates was found to reduce the residual concentrations of most metals.

Kuyucak (2006) concludes that factors governing the metal-removal process, in addition to the pH, include chemical reagents used and the oxidation/reduction and hydrolysis reactions, the presence of biotic and abiotic catalysts and the retention time of the effluent in the reactors.

5.3.1 Zinc

Zinc is always present in effluent water from steelworks and as described in Chapter 3, zinc is the only metal approaching the current consent limits at the Tata Port Talbot Steelworks final effluent discharge.

Onset of the zinc precipitation occurs at pH 7.6, but residual zinc concentrations of under 0.5 mg/l were only achieved at a pH above 9 (Swindley, 1998; Hartinger, 1994). According to Dyer et al. (1998) zinc hydroxide exemplified the significant impact of the solids phase’s crystallographic formation history on metal solubility. 7 distinct solids

phases have been identified for zinc hydroxide, but in industrial precipitation processes, the solubility of the amorphous form (amorphous $\text{Zn}(\text{OH})_2$) will most likely represent total Zn in solution since, at most, some hours will be available for any precipitate to form (Dyer et al., 1998). According to Swindley (1998) zinc precipitates as a cloudy white precipitate until higher pH values, when the structure of the precipitate was observed to change to a crystalline form. Changes of the physical characteristics of the precipitate were reported to occur on standing at pH between 10.5 and 11.

Table 5.4 Precipitation treatment results for zinc-containing wastewaters (Eckenfelder, 2000)

Source	Zinc concentration mg/l		Comments
	Initial	Final	
Zinc plating	---	0.2-0.5	pH 8.7-9.3
General plating	18.4	2.0	pH 9.0
	---	0.6	Sand filtration
	55-120	1.0	pH 7.5
	46	2.9	pH 8.5
		1.9	pH 9.2
		2.8	pH 9.8
		2.9	pH 10.5
Metal fabrication	---	0.5-1.2	Sedimentation
		0.1-0.5	Sand filtration
Radiator manufacture		0.33-2.37	Sedimentation
		0.03-0.38	Sand filtration
Blast furnace gas scrubber water	50	0.2	pH 8.8
Zinc smelter	744	50	
	1500	2.6	
Ferroalloy waste	11.2-34	0.29-2.5	
	3-89	4.2-7.9	
Ferrous foundry	72	1.26	Sedimentation
		0.41	Sand filtration
Deep coal mine – acid water	3.3-7.2	0.01-10	

Table 5.4, outlines results for total zinc concentrations achieved by zinc precipitation and in some cases further treatment for zinc-containing effluent in metal and mining industry. As seen in the table, zinc precipitation alone doesn't often achieve low levels of concentrations, but further sand filtration has been found to improve these results

5.3.2 Choice of a Precipitation Reagent

Although alkalis using hydroxyl group (OH^-) are most widely used reagents, several carbonate -containing alkalis are also used for precipitation reactions. Typically the choice of the alkali reagent used is made in terms of calcium or sodium and hydroxide or carbonates, although in some cases magnesium-based reagents are also used. According to Bullen (2006), the choice of chemical used is based on the rate and degree of required pH increase, solubility in water, handling and cost of reagent. The amount of alkali reagent required is usually greater than that predicted stoichiometrically and is controlled by rate of reaction, size of reaction vessels, and concentration of other elements (e.g. sulphate and carbon dioxide) present in the effluent (Bullen, 2006), but also the effluent temperature will have an effect on the metal solubility.

Table 5.5 Theoretical doses and costs of commonly used alkali reagents (Coulton et al., 2003b)

Reagent		Unit cost (£/tonne)	Theoretical consumption kg per kg Fe		Actual consumption kg per kg Fe		
			Dose	Cost	Efficiency	Dose	Cost
Calcium oxide	CaO	100	1.00	10 p	65%	1.54	15 p
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	100	1.33	13 p	65%	2.05	21 p
Magnesia	MgO	220	0.72	16 p	80%	0.90	20 p
Magnesium hydroxide	$\text{Mg}(\text{OH})_2$	260	1.04	27 p	80%	1.30	34 p
Sodium hydroxide	NaOH	260	1.433	37 p	95%	1.50	39 p
Sodium carbonate	Na_2CO_3	150	1.89	28 p	95%	2.00	30 p

The costs involved in using different alkali reagents vary considerably as can be seen in Table 5.5, which outlines the theoretical doses and costs for commonly used alkali reagents. The table has used reagent kg per kg of Fe as the consumption indicator as Fe is often present when treating metal -containing waters, such as acid mine drainage.

The table gives nevertheless a good idea of the chemical costs involved in using different reagents.

As seen in Table 5.5, out of the commonly used alkali reagents calcium oxide, magnesia and calcium hydroxide are the cheapest. Limestone is readily available within the soil in most parts of the World and as seen in the Table, calcium costs are generally lower than sodium products and the cost savings often lead to calcium products being used for the treatment of high flows with high metal loads (Bullen, 2006). When sulphate is present in high enough concentrations in the effluent, gypsum can however be formed when calcium products are used and calcium based alkali reagents require lime slaking and dosing equipment, which involve increased capital expenditure. The sodium and magnesium –based alkalis are however more expensive, so a careful assessment of capital (CAPEX) and operational cost (OPEX) involved should be carried out prior to making the choice for the alkali reagent. Table 5.6 gives an overview of the factors influencing selection between calcium or sodium compounds for minewater treatment.

Table 5.6 Factors influencing the selection of calcium or sodium compounds for minewater treatment (modified from Skousen, 1988; Bullen, 2006; Kuyucak, 2006)

Factor	Calcium	Sodium
Solubility	Slow	Fast
Application	Requires mixing	Diffuses well
Hardness	High	Low
Gypsum formation	Yes	No
Calcium carbonate formation	Yes	No
Chemical cost	Low	High
Health and Safety issues	Lower	Higher
Maintenance costs	Higher	Lower
Amount of sludge generated	Higher	Lower
Sludge settles	Faster	Lower
CAPEX	Higher	Lower
OPEX	Lower	Higher

5.4 Laboratory Studies - Precipitation and Co-precipitation Experiments

In order to better understand the metal removal mechanism for complex mixtures of metals often found in steelworks final effluent discharge, a series of batch laboratory experiments were carried out in order to study the precipitation of zinc, nickel, copper, iron, cadmium and lead and co-precipitation of zinc with nickel, copper, iron, cadmium, chromium and lead using base titration with sodium hydroxide (NaOH).

Titration were carried out using Cardiff tap water into which the chemical reagents were allowed to dissolve naturally at room temperature. The first sample was taken at the pH to which the solution settled naturally, at anywhere between pH 6 and around pH 7.5. The second sample on the other hand was taken on pH 8, except with copper, with which the second sample was taken at pH 7 due to very strong solubility of copper prior to pH 8.

The purpose of the titrations was to establish the behaviour of the metal ions during precipitation and co-precipitation, whilst determining the pH range where minimum solubility occurs. The dependence of solubility on pH was studied by precipitating and co-precipitating a series of samples at different pH's, followed by filtering the solution and analysing the sample by using inductively coupled plasma spectrometry to determine the residual soluble metal concentration.

5.4.1 Experimental Solutions

A series of experiments were designed in order to examine the behaviour of metal ions and metal ion interactions during hydroxide precipitation. The combined neutralisation of metal ions offers an opportunity for different residual solubility and possible surface adsorption through co-precipitation. The beneficial or detrimental effects of co-precipitation can be then compared to a single metal ion precipitation.

In this laboratory study a 100 mg/l metal concentration or in the case of co-precipitation a 2 X 100 mg/L of metal concentration was added to a litre of tap water to create a solution. The single and co-precipitation metal ion combinations are shown in Table 5.7. As seen in the Table, the double metal ion combinations were especially concentrating in zinc.

Table 5.7 Single and co-precipitation metal Ions

Zn	Fe	Cu	Ni	Pb	Cd
Zn/Fe	Zn/Ni	Zn/Cr	Zn/Cu	Zn/Cd	Zn/Pb

Stock solution of metal chlorides and sulphates were prepared using General Purpose Reagent and AnalaR -grade metal solutions (Table 5.8) and tap water in 1000 ml volumetric flasks. All the metal ions, except for chromium were in valance two as can be seen in Table 5.8 below.

Table 5.8 Reagents for stock solutions

Metal Ion	Chemical	Formula
Zn^{2+}	Zinc Sulphate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
Cu^{2+}	Copper II Sulphate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Ni^{2+}	Nickel Chloride	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
Pb^{2+}	Lead Chloride	PbCl_2
Fe^{2+}	Iron II Sulphate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Cd^{2+}	Cadmium Sulphate	$3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$
Cr^{6+}	Potassium Dichromate	$\text{K}_2\text{Cr}_2\text{O}_7$

0.5M sodium hydroxide solution was prepared by addition of 20g of AnalaR sodium hydroxide (NaOH) pellets to one litre of tap water in a volumetric flask.

5.4.2 Sodium Hydroxide Titrations

Titration were performed using sodium hydroxide with single and double metal ion combinations. 1000 ml metal ion solutions were prepared by adding the correct quantities of metal stock solution and making up the solution to a volume of 1000 ml. The solution was transferred to a beaker and placed on a magnetic stirrer, set to a half

speed with an octahedral magnetic flea. The solution was left until the pH had stabilised, after which the experiments was commenced.

With most of the precipitation and co-precipitation experiments, the first samples were taken at pH 7 or lower if the solutions stabilised naturally to a lower pH. However, this was not the case with a few of the metals as after stabilising, their initial pH was already higher to that of 7. The original pH's of the metals and metal combinations can be seen in Table 5.9.

Table 5.9 The starting pH of the precipitation and co-precipitation experiments

Metal(s)	Zn	Zn/Fe	Zn/Cu	Zn/Ni	Zn/Cd	Zn/Pb	Zn/Cr	Fe
Original pH	7.25	6	6.2	7.2	6.4	6.2	6.4	7.6
Metal(s)	Cu	Cu/Zn	Ni	Ni/Zn	Pb	Pb/Zn	Cd	Cd/Zn
Original pH	6.4	6.22	7.8	7.4	7.0	7.0	7.4	6.4

The volumes of 0.5 M sodium hydroxide (NaOH) required to raise the pH to stable 7, 8, 9, 10 and 11 were measured. Furthermore, a sample was taken at each pH and filtered through a 0.4 µm filter for analysis of remaining soluble metal concentration in solution using a Perkin Elmer Optima DV2100 Inductively Couple Plasma (ICP) atomic emission spectrometer. The technicians (Jeff Rowlands and Ravi Mitha) at the Characterisation Laboratories for Environmental Engineering Research (CLEER) facility in the School of Engineering at Cardiff University carried out the chemical analyses. The pH meter used in the study was Hanna HI208.

5.5 Theoretical Prediction with PHREEQC

PHREEQCi Version 2 (Parkhurst, D.L. et al., 1999) is a “free-ware” computer program written in the C programming language that is designed to perform a wide variety of low-temperature aqueous geochemical calculations, based on an ion-association aqueous model.

Theoretical prediction for single-metal precipitation was carried out by Dr Devin Sapsford from Cardiff University School of Engineering in order to compare the results

of the precipitation and co-precipitation experiments against theoretical values. The metal ions predicted by PHREEQCi included Zn, Fe, Cu, Ni, Pb and Cr.

Further, experimental precipitation and co-precipitation results have been converted into logarithmic metal concentration ($\log [Me_{z+}]$) values according to Equation 2 and compared to the predicted PHREEQCi 2 values.

The effect of pH on the solubility of the metals is presented as a graph of logarithmic metal concentration; $\log [Me_{z+}]$ based on the Equation (2):

$$\log [Me_{z+}] = \log K_{sp} + zK_w - zpH \quad (2)$$

Where:

$K_{sp} = [Me_{2+}]/[H^+]^2$ (solubility product constant)

zK_w = equilibrium constant for the relevant metal

5.6 Results

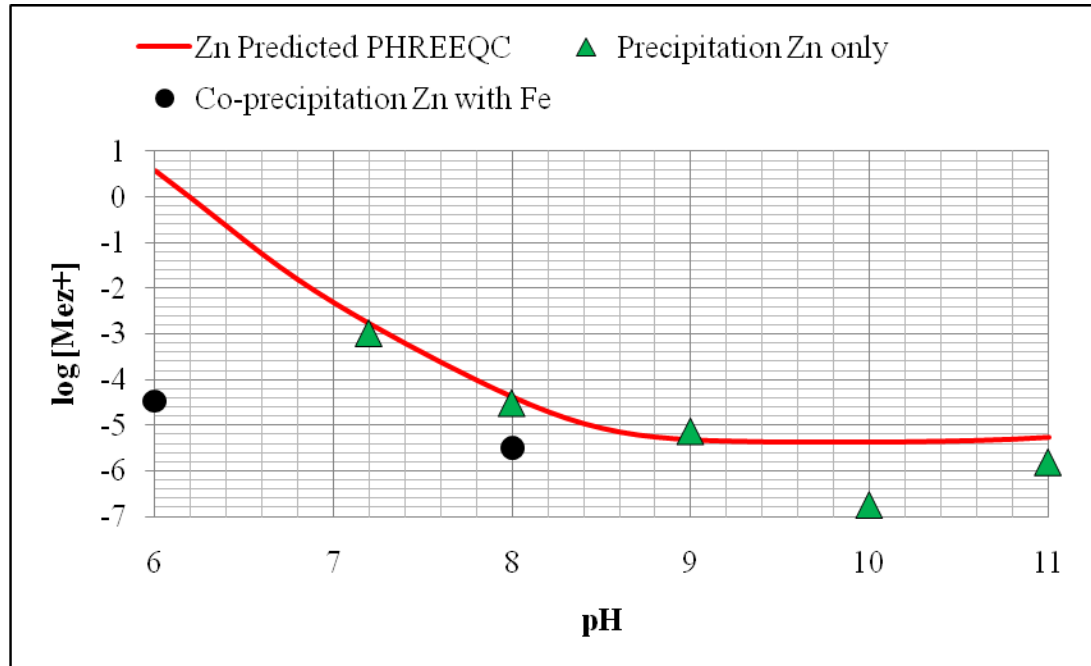
The results compare how the theoretical metal solubility results from PHREEQCi 2 compare with experimental precipitation and co-precipitation solubility results. Within the following graphs, the PHREEQCi 2 results are outlined in red lines, where as the experimental precipitation and co-precipitation results are shown in scatter format.

Next to the PHREEQCi zinc theoretical prediction, the first six graphs outline experimental zinc precipitation results in relation to the experimental zinc co-precipitation results with iron, copper, nickel, cadmium, lead and chromium. The following five graphs outline PHREEQCi theoretical values for Fe, Cu, Ni, Pb and Cr, together with their experimental precipitation and co-precipitation results.

5.6.1 Zinc Precipitation and Co-precipitation Results

As seen in Figure 5.2, as a single element, the zinc precipitation results follow predicted PHREEQC values closely at pH's 7 to 9 and give even lower concentration values at pH's 10 and 11. When it comes to solubility, PHREEQCi data for zinc indicate that the best theoretical solubility is between pH 9.5 and 10 and the experimental zinc

precipitation curve is also at its lowest point at pH 10, although the concentrations left in solution are over ten times higher than predicted by PHREEQC. These results support the finding of Swindley (1999) and Hartinger (1994), which indicate that lowest; under 0.5 mg/L residual zinc concentrations were achieved via precipitation at pH 9 or above. Around the pH 8.5, these results resemble closely the performance of



the steelworks final discharge precipitation and settlement system for zinc left in solution, although it is clear that lower concentrations of zinc are predicted by PHREEQC and achieved by laboratory experiments than in the field.

Figure 5.2 Comparison of theoretical PHREEQC Zn concentrations, experimental Zn precipitation and Zn/Fe co-precipitation results at various pH's

When co-precipitating with iron II, zinc precipitation values were well under the predicted value at pH 6 and up to ten times less at pH 8. At pH's 9 to 11, there was no Zn left in the solution when co-precipitating with soluble iron II. This would indicate that the precipitation of zinc at the presence of iron would enhance the residual concentrations of zinc in solution.

As can be seen in Figure 5.3, when co-precipitating with copper, zinc precipitation results were close to the theoretical at pH 8-9, although the values were found to be higher than the predicted by PHREEQC. At pH 6.2, the zinc values were much lower while co-precipitating with copper, than predicted by PHREEQC. When co-

precipitating with copper, the best zinc solubility is achieved at pH 11, where the concentration of zinc in solution is below the instrument detection limit.

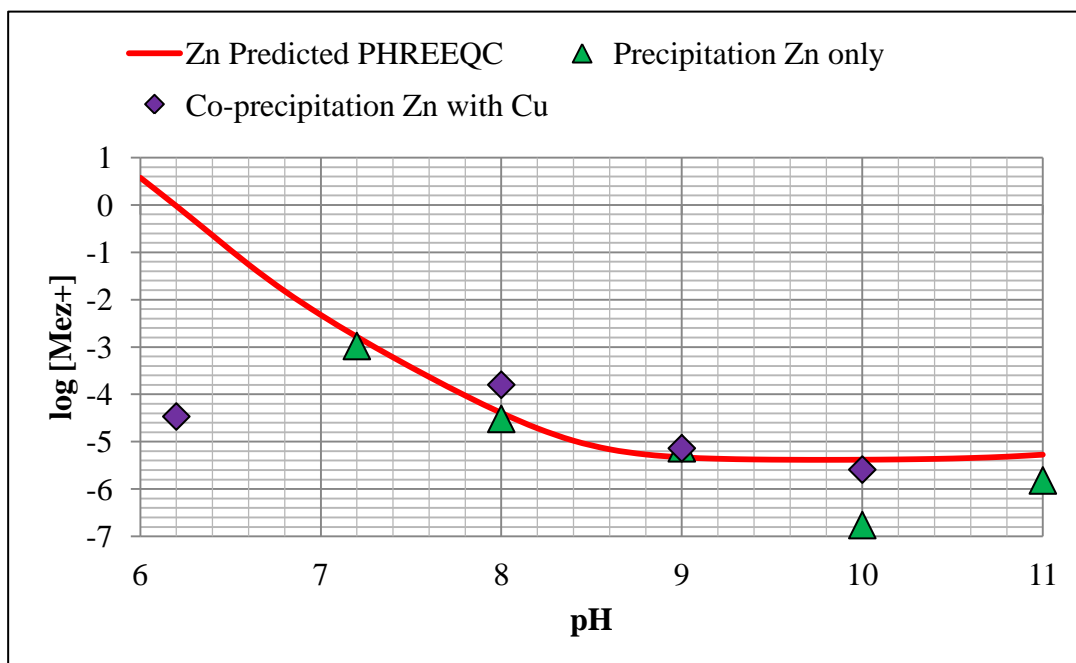


Figure 5.3 Comparison of theoretical PHREEQC Zn concentrations, experimental Zn precipitation and Zn/Cu co-precipitation results at various pH's

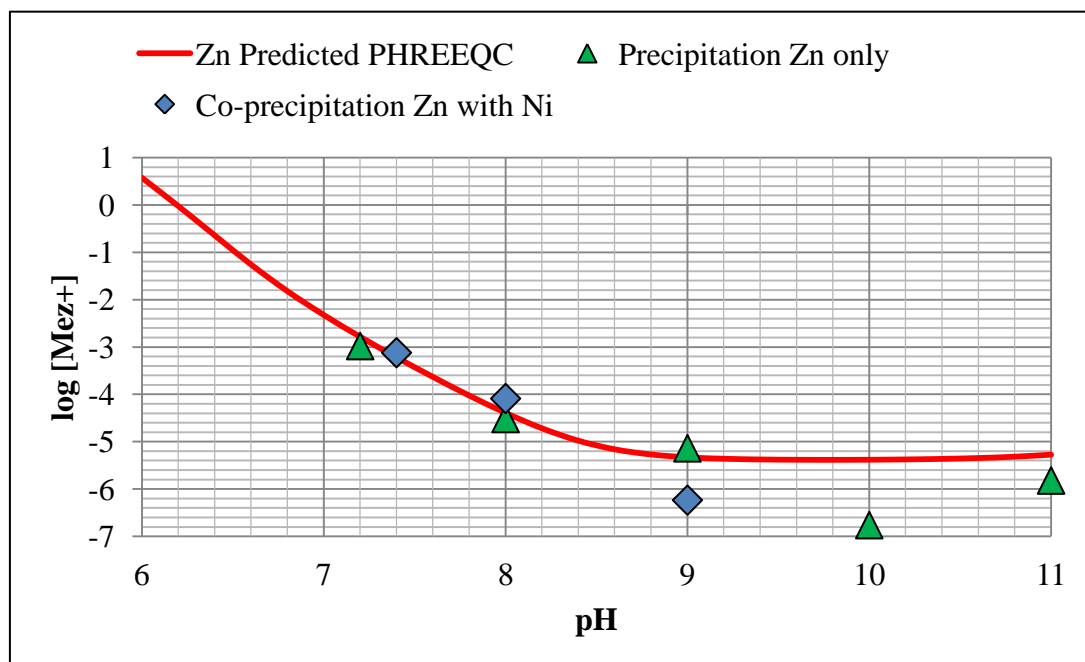


Figure 5.4 Comparison of theoretical PHREEQC Zn concentrations, experimental Zn precipitation and Zn/Ni co-precipitation results at various pH's

Experimental zinc co-precipitation in the presence of nickel resulted in higher concentrations at pH 7 and 8 than either the zinc precipitation results or the PHREEQC theoretical data (Figure 5.4). At pH 9 the co-precipitation achieved lower concentrations than the PHREEQC or the precipitation results and after pH 9 there was no zinc concentration left in solution at all. The zinc co-precipitation results with nickel indicate that nickel enhances zinc precipitation after pH 9.

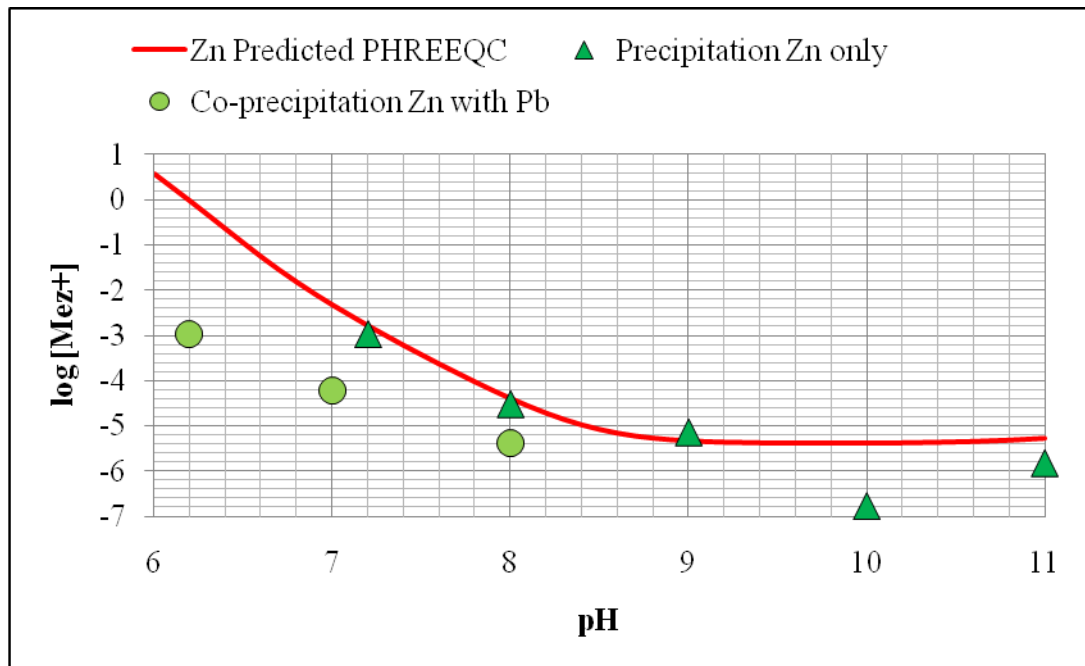


Figure 5.5 Comparison of theoretical PHREEQC Zn concentrations, experimental Zn precipitation and Zn/Cd co-precipitation results at various pH's

As seen in Figure 5.5, the co-precipitation of zinc with cadmium follows very similar metal concentration patterns as the predicted theoretical zinc concentrations with PHREEQC and zinc precipitation on its own at all pH's, except pH 10. At pH 8 and 11 the co-precipitation of zinc is almost identical to the zinc precipitation results. It appears that the presence of cadmium does not seem to affect the zinc precipitation majorly.

As seen in Figure 5.6 zinc co-precipitation in the presence of lead gives considerably lower zinc concentrations at pH 6-8 than theoretical or experimental zinc precipitation and leaves no detectable zinc concentrations in solution beyond pH 8. Despite the much lower concentrations, the zinc co-precipitation in the presence of lead provides results that follows the zinc and theoretical precipitation results curve well at pH 6-8. At pH's

9-11 zinc co-precipitation at the presence of copper results in concentrations below detection limit.

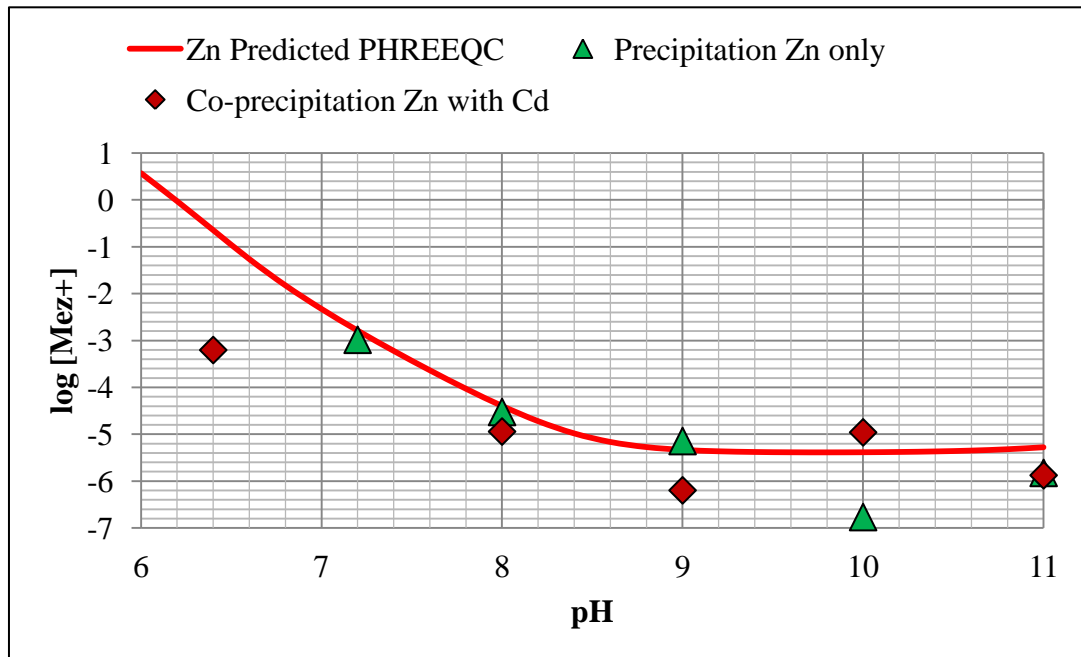


Figure 5.6 Comparison of theoretical PHREEQC Zn concentrations, experimental Zn precipitation and Zn/Pb co-precipitation results at various pH's

Zinc co-precipitation in the presence of chromium (Figure 5.7) gives similar results and trends as theoretical PHREEQC predicted values at pH 8-11. On the other hand, the zinc co-precipitation doesn't give as good solubility results than does the precipitation of zinc on its own. Both, the precipitation and co-precipitation do nevertheless give their minimum solubility at around pH 10, similarly to the theoretical the PHREEQC values.

Metal finishing uses large amounts of chromium. Chromium is commonly present in the steelworks pickling lines as hexavalent chromium in the form of chromium trioxide (CrO_3). The chromium used on the co-precipitation experiments was also a hexavalent chromium compound, which in itself does not precipitate out of solution. Therefore the chromium concentrations were not tested as a part of the Zn/Cr co-precipitation. Zinc levels were tested nevertheless to find out how the presence of the hexavalent chromium will affect zinc precipitation. In order to remove chromium via precipitation, it needs to be first reduced to trivalent chromium by using, for example, chemical reducing agents.

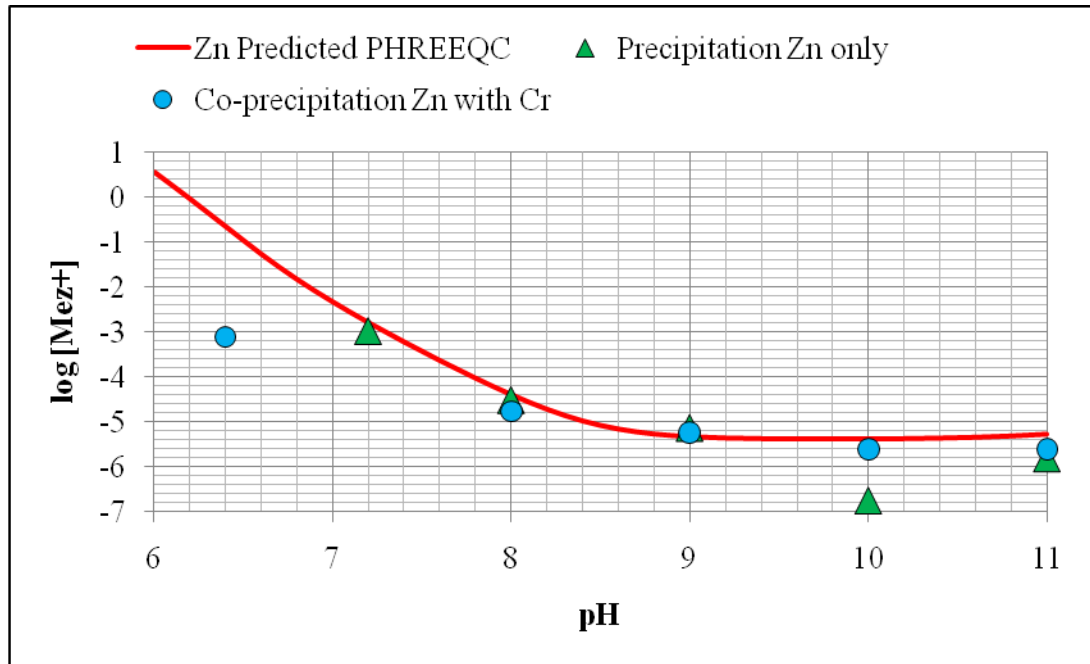


Figure 5.7 Comparison of theoretical PHREEQC Zn concentrations, experimental Zn precipitation and Zn/Cr co-precipitation results at various pH's

As a part of the zinc precipitation and co-precipitation experiments, concentrations of the other metals listed in Table 5.7 and 5.8 were also looked at during the precipitation and co-precipitation experiments. The results of these precipitation and co-precipitation experiments are presented in the following sections.

5.6.2 Copper Precipitation and Co-precipitation Results

In Figure 5.8 the results of copper precipitation data as predicted by PHREEQC is compared with experimental copper precipitation and copper co-precipitation results at the presence of zinc.

For both the copper precipitation as a lone metal and the copper co-precipitation with Zn, no detectable concentrations of copper are left in solution beyond pH 7. The PHREEQC prediction, albeit very low, does indicate there should be some, although very small, concentration of copper left in solution even beyond pH 7, with the solubility curve achieving its lowest point around pH 9.5.

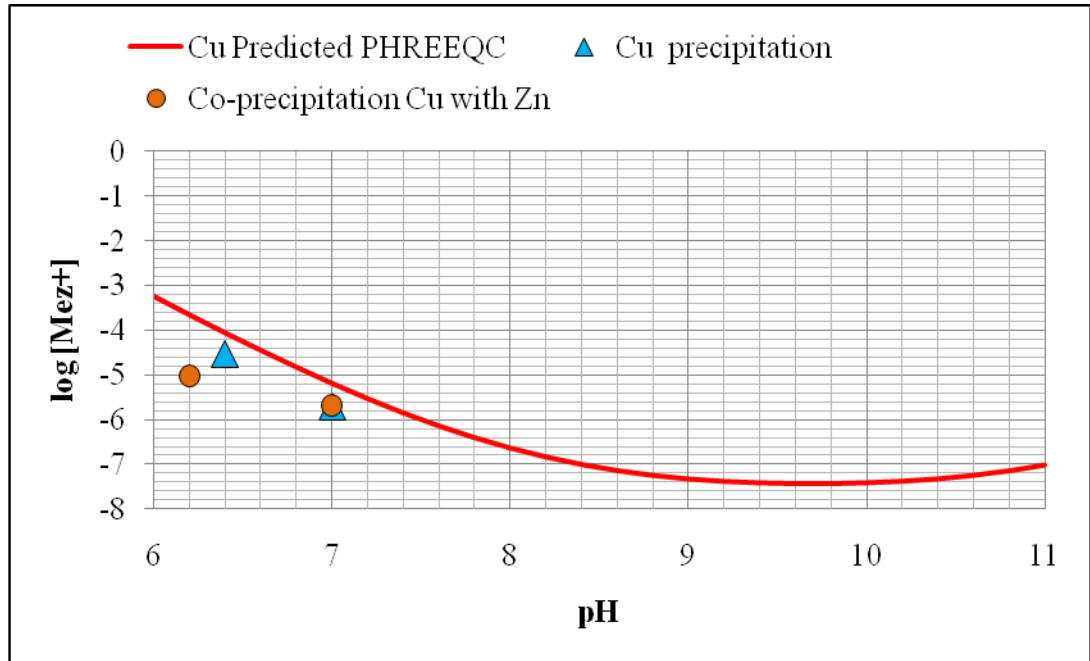


Figure 5.8 Comparison of theoretical PHREEQCi Cu concentrations, experimental Cu precipitation and Cu/Zn co-precipitation results at various pH's

5.6.3 Nickel Precipitation and Co-precipitation Results

Nickel precipitation and co-precipitation results (Figure 5.9) follow the trend of the predicted PHREEQCi values with the co-precipitation achieving little better results than nickel precipitation alone. These results support Hartinger (1994), who reported residual concentrations of nickel decreasing when co-precipitating with zinc. At pH below 7.4 nickel co-precipitation and precipitation appear to achieve nevertheless lower nickel concentrations than PHREEQCi indicates. Beyond pH 10, there are no detectible concentrations of nickel left in solution by neither precipitation nor co-precipitation with zinc, although PHREEQCi indicates low concentrations present in solution. It is possible that this is an incorrect result and there should be some residual concentrations, above the detection limit present in the solution.

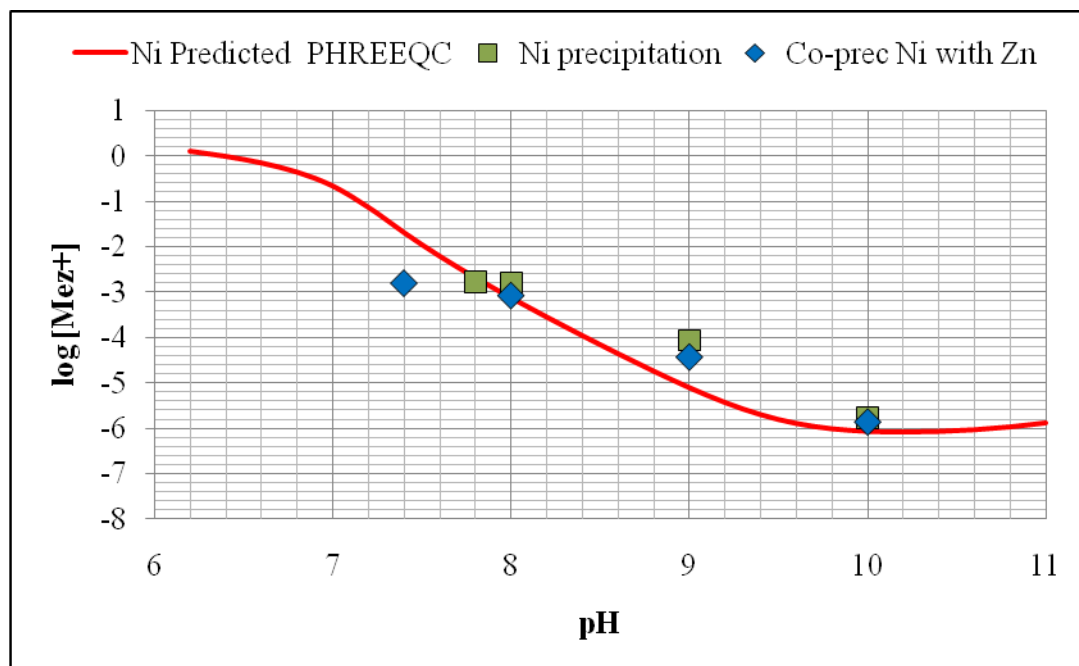


Figure 5.9 Comparison of theoretical PHREEQC Ni concentrations, experimental Ni precipitation and Ni/Zn co-precipitation results at various pH's

5.6.4 Lead Precipitation and Co-precipitation Results

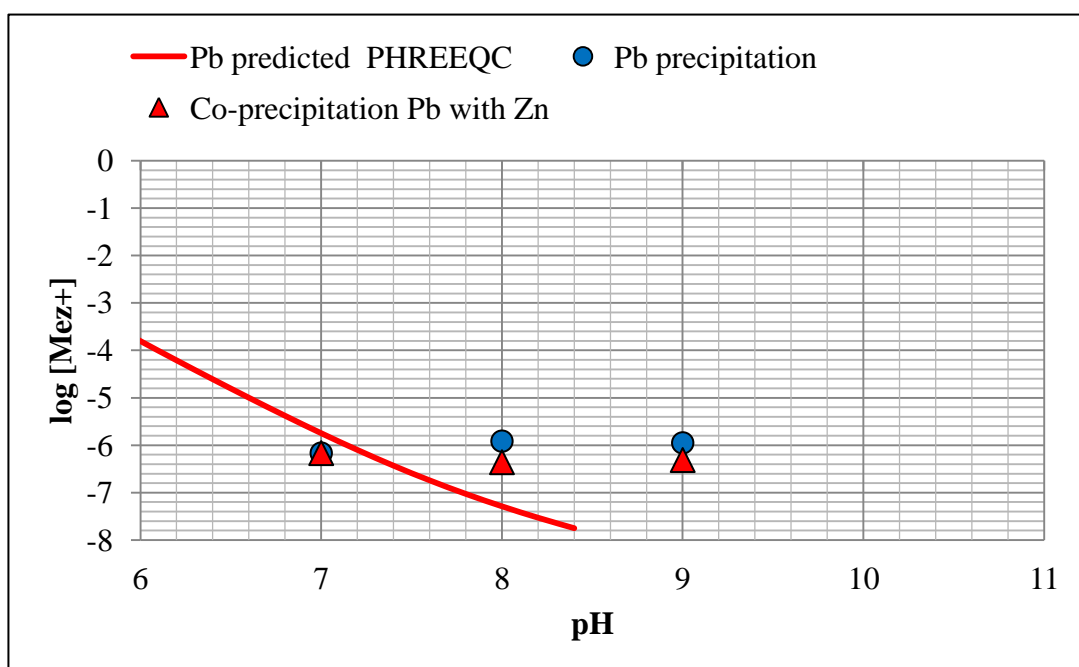


Figure 5.10 Comparison of theoretical PHREEQC Pb concentrations, experimental Pb precipitation and Pb/Zn co-precipitation results at various pH's

Lead is the only metal out of those tested, where the PHREEQCi predictions of the soluble metal concentrations are generally lower than what was achieved in laboratory experiments by lead precipitation and co-precipitation. Furthermore, PHREEQCi predicts that the lead concentrations left in solution beyond pH 8.4 are below log-8. Lead precipitation and co-precipitation concentrations follow each other closely in pH 7-9 and in both cases no detectible concentrations are left in solution beyond pH 9.

5.6.5 Iron Precipitation and Co-precipitation Results

During iron co-precipitation, no detectible concentrations are present in the solution at any tested pH. Both iron precipitation and PHREEQCi theoretical values (Figure 5.11) on the other hand, although clearly apart, indicate a similar trend with the minimum solubility of iron between pH 10 and 10.5. Iron precipitation and PHREEQCi values come closest at pH 10, but at pH 11 PHREEQCi gives no theoretical values, indicating no iron left in solution. Perhaps no data exists within the PHREEQC software beyond pH 10.8 for iron precipitation. It should also be noted that much lower solubilities are achieved for iron if it is oxidised to a higher valance to iron III. This phenomenon will be explained in more depth within Chapter 6.

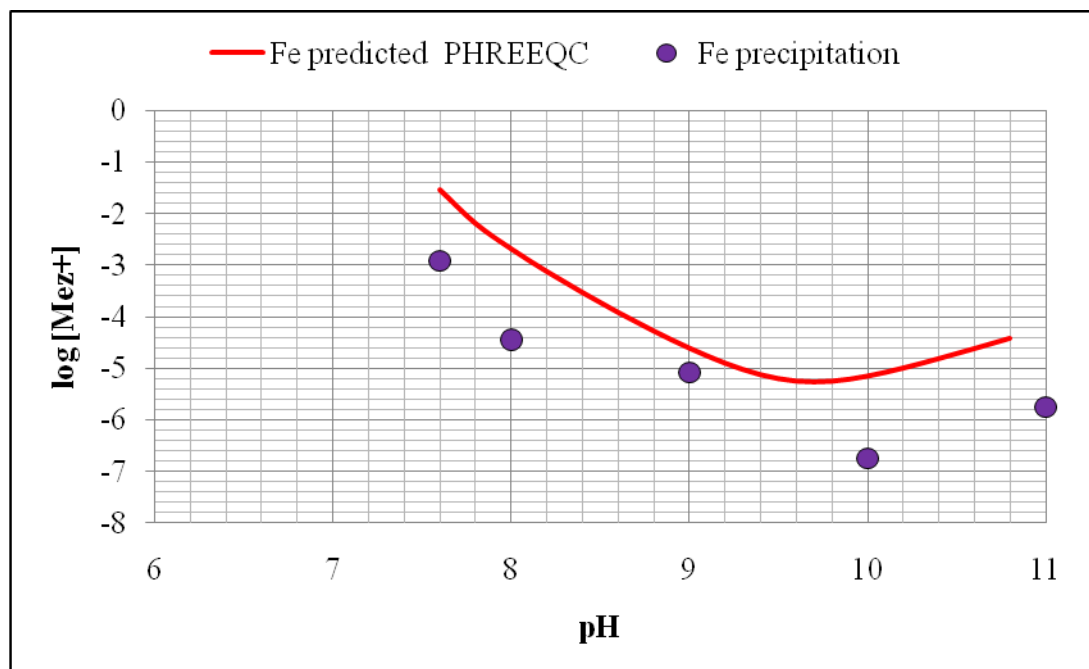


Figure 5.11 Comparison of theoretical PHREEQCi Fe concentrations, experimental Fe precipitation results at various pH's

5.6.6 Cadmium Precipitation and Co-precipitation Results

Precipitation and co-precipitation results for cadmium (Figure 5.12) in the presence of zinc both follow similar a trend to the PHREEQCi predicted values, but interestingly on the opposite sides of the PHREEQCi curve. Cadmium precipitation is achieving higher solubility results, although the precipitation and co-precipitation values are getting closer together from pH 8 to 10. PHREEQCi predicts no concentration values beyond pH 9.8, but precipitation and co-precipitation results both show some metal concentrations at pH 10.

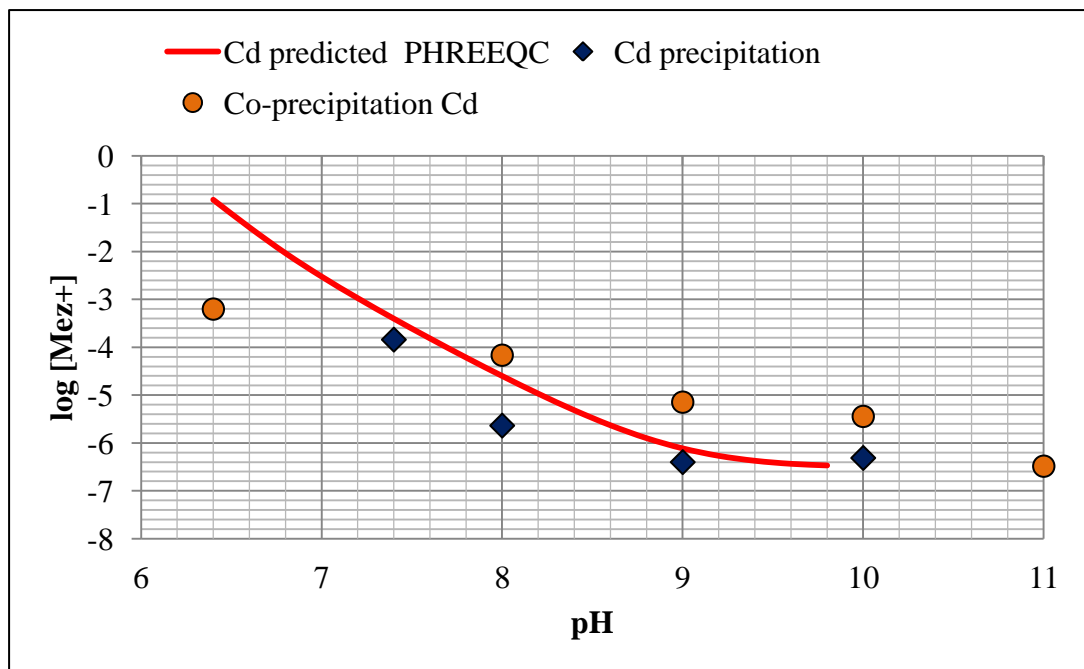


Figure 5.12 Comparison of theoretical PHREEQCi Cd concentrations, experimental Cd precipitation and Cd/Zn co-precipitation results at various pH's

5.7 Conclusion

Hydroxide is the most commonly used ion for chemical precipitation.

PHREEQCi 2 theoretical and the experimental soluble metal concentrations match quite well through the various pH's.

PHREEQCi 2 indicates that the minimum zinc solubility is received at pH 9.5. Laboratory experiments support this.

The co-precipitation results support previous work by Swindley (1999), which showed that the actual solubility of metal ions and the minimum pH for maximum precipitation varies according to the mix of metal ions present in the solution.

Iron enhances zinc precipitation strongly via co-precipitation. A similar effect, although to a lesser extent, is achieved zinc co-precipitation with nickel and lead.

6 FORMATION OF HIGH DENSITY SLUDGE FROM STEELWORKS EFFLUENT

6.1 Introduction

As discussed in Chapter 5, conventional precipitation is effective in removing metals from solution and there are valid reasons for using chemical precipitation, which is easy to manage and predict and reagents, especially lime, are widely available, inexpensive and easily handled. This type of treatment does however lead to the need to dispose of metal-rich sludges resulting from the treatment of the effluents. Common with most effluent plants of this type, especially when sodium hydroxide is the alkali of choice, the settled sludge solid concentrations are very low. In many similar situations the so-called High Density Sludge (HDS) process has been found to be highly effective at improving sludge quality and enhancing sludge dewatering behaviour. The HDS process, where precipitates are recycled to mix with the incoming feed, is a mechanical and chemical technique used to improve the physical properties of the sludge. The prior precipitated sludge is either mixed with alkali prior to adding the incoming effluent or it's mixed with the effluent prior to adding the alkali, depending on the type of high density sludge process chosen. The recycling of the previously precipitated sludge will result in solids crystallisation, creating denser, heavier sludge particles than the ones achieved by conventional precipitation process.

Upgrading the existing conventional precipitation and neutralisation treatment plant to High Density Sludge (HDS) process may not only improve the sludge settling and dewatering characteristics (Dey et al., 2007), but results in additional improvement in water quality, increased reagent efficiency, reduced overall treatment costs (Cox et al., 2006) and reduced clarifier size (Kuyucak et al., 2001).

Use of the (HDS) process started in the steel industry looking at treatment of acidic pickle liquor, which is used for removing surface impurities from steel. HDS has been widely recognised as the preferred treatment methods for mine water, especially Acid Mine Drainage (AMD), which contains high metal concentrations. No previous studies have been carried out looking at the performance of the high density sludge process in

treating non-acidic, high volume effluents with low metal concentrations such as final effluent born in the steelworks.

6.2 Types of Treatment Processes

Three typical treatment processes, namely basic or bond (tailings or sludge bond) treatment, conventional treatment and HDS processes are used extensively in industry for treatment of metal-containing wastewaters and have been described in detail by Vachon et al., 1987 and Zinck et al., 1997. The common and basic treatment methods are often also referred to as to low density sludge (LSD) processes.

6.2.1 Conventional wastewater treatment system

Conventional single-pass wastewater treatment system (Figure 6.1) remains to date the most common way of treating metal-containing effluents. In a conventional treatment plant, the precipitation is carried out in a mix tank with a controlled additional of alkali reagent in order to attain the desired pH setpoint. Arisen slurry is then contacted with a flocculant either at the clarifier feed well or prior to that in order to enable liquid/solid separation within the clarifier. The sludge is collected from the bottom of the clarifier and is either pumped to, for example, a sludge bund for dewatering and/or storage or it is send to a filter-press, centrifuge or similar for further dewatering.

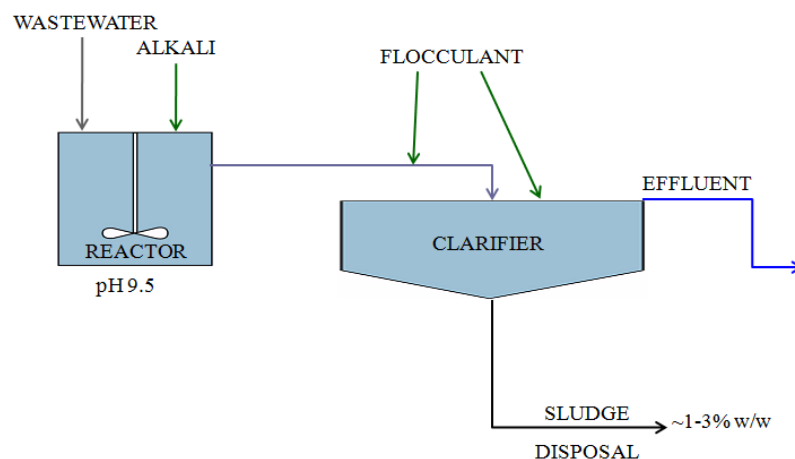


Figure 6.1 Conventional precipitation by single-pass wastewater treatment systems

The single-pass treatment system has low capital and operational costs and often achieves metal concentrations below the local consent requirements. This type of treatment system does however create bad quality sludge with low settling rates and filtrations characteristics, together with low solid concentrations % (w/v)¹³, resulting in high operational costs for sludge dewatering and disposal and loss of valuable fresh water with the sludge.

Conventional precipitation can also be carried out as a multi-step neutralisation process (Figure 6.2), where lower concentrations of metals are required for the treated water or a precipitation of certain elements is required prior to the precipitation of the remaining metals. This is the case when treating for example arsenic (As) –containing waters, where the pH of the first reactor is kept low at around pH 4.5 in order to enable precipitation of arsenic often as a co-precipitation with ferric or ferro-reagents, prior to rising to pH 9.5. It is also common with a conventional treatment system; despite whether a one or multi-step neutralisation is in use, that air is introduced to the reactor(s) to help oxidation of Fe^{2+} to Fe^{3+} . This helps to produce chemically more stable sludge (Kuyucak et al., 1995).

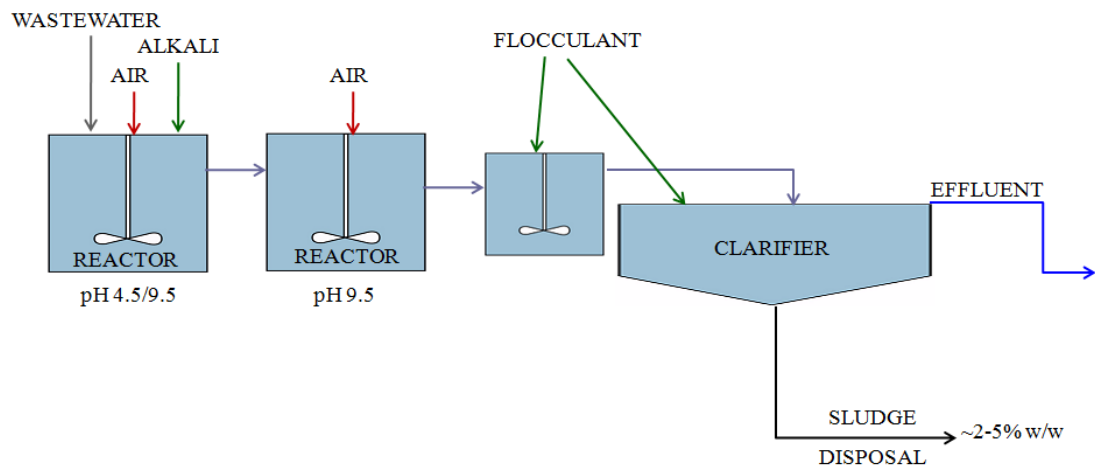


Figure 6.2 Conventional precipitation by multi-step neutralisation treatment system

¹³Sludge solid concentrations are either expressed as % (w/v) for number of grams material (solid or liquid) per 100 ml of the final solution or as % (w/w) for number of grams material (solid or liquid) per 100 g of the final solution

In comparison to the single-pass treatment system, a multi-step neutralisation does achieve sludge concentrations (Figure 6.2) that are often a little higher, up to 5% (w/v) (Aubé et al; 2003; Aubé, 2004) than what is achieved by a single-pass systems with only one reactor.

6.2.2 Simple Sludge Recycle Process

It is possible to get a step closer to HDS process treatment system by recycling the sludge back to the reactor in a single-step precipitation system (Figure 6.3). This process has not yet been patented and its benefits over the conventional treatment system have not been published. It is however, used regularly in industry. In the simple sludge recycle process, the sludge from the bottom of the clarifier is recycled to the reactor as seen in Figure 6.3. This process has a number of advantages over the conventional treatment, including (Aubé, 2004):

- Reduced scaling,
- Improved solid/liquid separation,
- Reduced reagent consumption and
- Increased sludge density up to 15% (w/v).

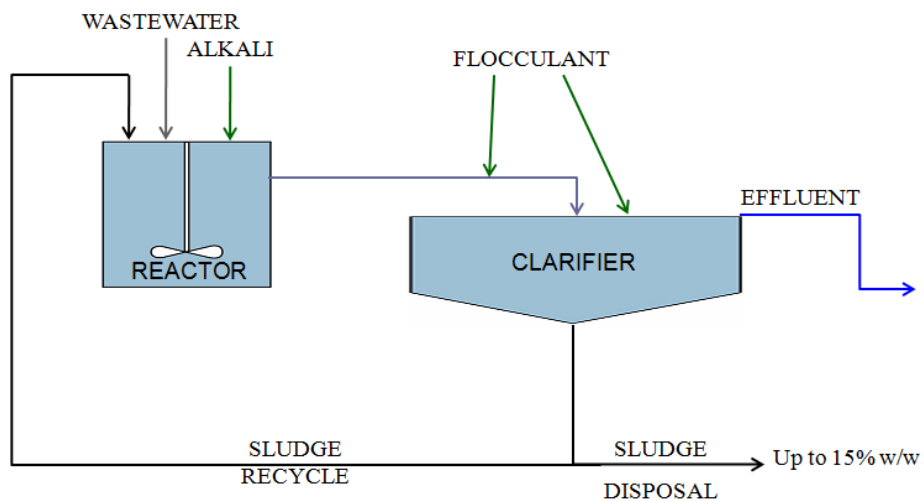


Figure 6.3 Simple sludge recycle process

6.2.3 High Density Sludge (HDS) Processes

HDS process is a mechanical technique used for improving the physical properties of the sludge and its also known as the state-of-the-art lime neutralisation process (MEND 1994; Kuyucak, 2006).

According to Kuyacak (2006), in order for a treatment plant to qualify for a HDS process, three conditions must be fulfilled, namely:

- More than one reactor is used to perform the neutralisation
- Portion of the sludge is recycled from the clarifier back to the reactors and
- Alkali is used as a reagent.

6.2.3.1 Conventional HDS Process

The first recorded HDS process was implemented in Bethlehem Steel Corporation (BSC) works in the late 1960's (Kostenbader et al., 1970). The BSC HDS process is based on the conventional HDS process and is outlined in a US patent 3738932 filed in April 1971 (Kostenbader, 1973). The conventional HDS process was originally invented for the treatment of pickle liquor (Haines et al., 1968), but was quickly adopted for other acidic waters containing metals, especially acid mine drainage. The conventional HDS process is applied at numerous mine sites throughout Canada, including Teck-Cominco's Sullivan Site, Cambior's La Mine Doyon and Noranda's Brunswick and Heath Steele mines (Zinck, 2005).

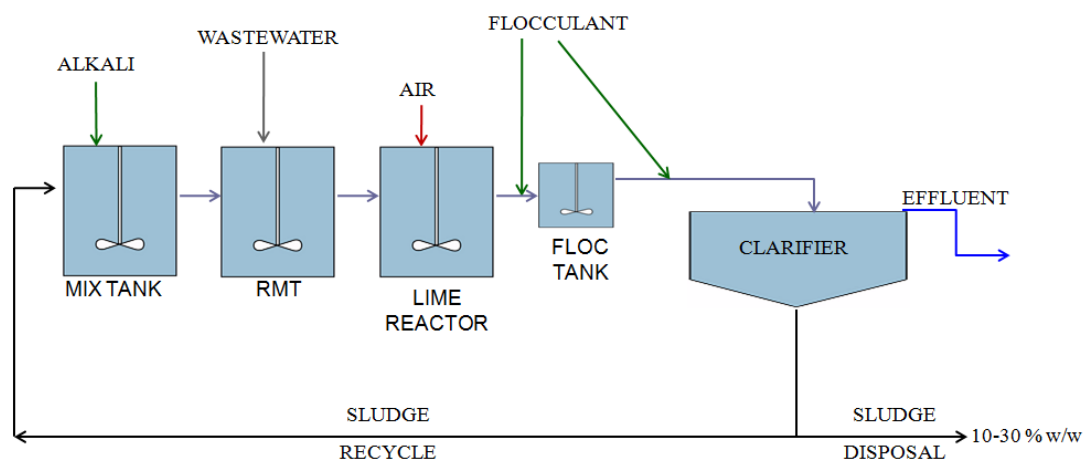


Figure 6.4 Conventional HDS process (Aubé et al, 2003)

In the conventional HDS process (Figure 6.4), the sludge is mixed with alkali in order to create lime/sludge slurry prior to feeding it to a Rapid Mix Tank (RTM), where the wastewater is added and mixed together with the lime/sludge slurry. The RMT is often used to offer better pH control within the process (Zinck, 2005). Within this setting, the air is added to the lime reactor to enable Fe^{2+} oxidation. It is common in the HDS process that the neutralisation reactors are aerated to oxidise Fe^{2+} and pH is continuously monitored. The arisen precipitate is flocculated with a polymer and a clarifier/thickener unit is used for liquid-solid separation. A portion of the generated sludge is recycled from the clarifier/thickener underflow back to process. The amount of sludge recycled is controlled by the sludge recycled ratio i.e. the ratio of solids recycled in relation to the amount of new solids precipitated and it is typically 20 to 30 kg of recycled solids per kg of new solids precipitated from the wastewater (Bullen, 2006). The recycled sludge is used as an additional alkali reagent as well as a platform for the arisen precipitate to attach to. The conventional HDS process outlined in Figure 6.4 was the original CESL (Cominco Engineering and Services Limited) design (Kuit, 1980), which was modified by Aubé et al. (2003).

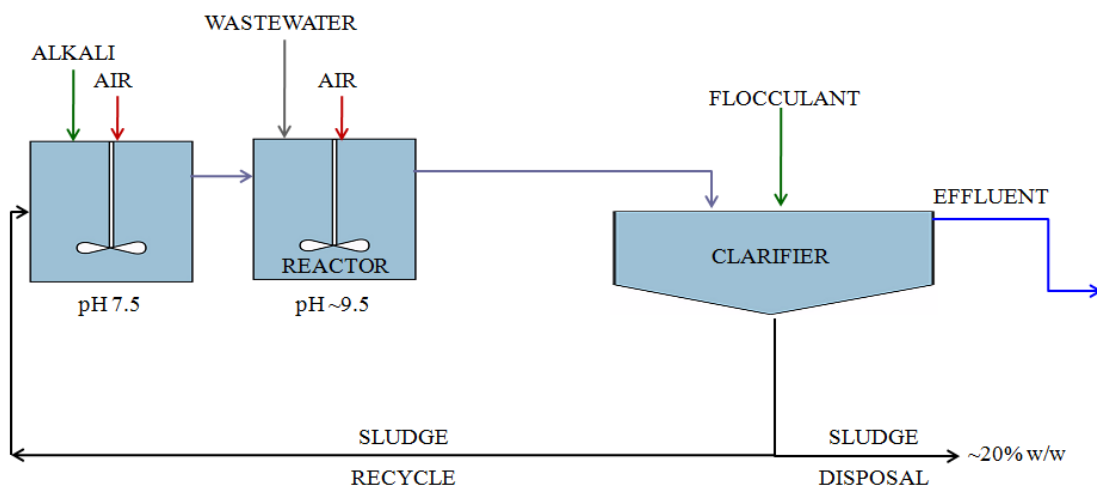


Figure 6.5 Heath Steele modified HDS process arrangement (Aubé, 2004)

Figure 6.5 shows Noranda Inc., Heath Steele Division recent variant of the HDS process. The Heath Steele HDS process is identical in concept and provides the same physical and chemical advantages as the HDS but without two (rapid mixing tank and flocculant tank) of the four reactors. With today's advanced process control systems, a Rapid Mix Tank is not necessary for pH control and gives no advantage as proven by pilot scale tests carried out by Aubé (2004).

6.2.3.2 Staged HDS Process

Although many different configurations of the HDS process has been trialled and used over time, only two main types of High Density Sludge (HDS) processes exist. As described in section 6.2.3.1 of this Chapter, in the conventional High Density Sludge (HDS) process the recirculated sludge is mixed with alkali reagent prior to introducing the minewater (Aubé et al., 2003). This type can also be called the Type I HDS process (Bullen, 2006). In the second HDS process, the minewater is mixed with sludge at the first stage reactor, prior to adding the alkali reagent. This process has been given many different names, including staged HDS process (Kuyucak et al., 1995), two-step HDS process (Kuyucak, 2006) and Type II HDS process (Bullen, 2006).

In the staged HDS process (Figure 6.6) the pH of the wastewater is arisen to a pH between 7.0 and 8.0 with the recycled sludge in the first reactor, depending on minewater chemistry and recirculation rates, resulting in the removal of a high proportion of the metals from solution (Aubé et al., 1997; Bullen, 2006). The pH in the first reactor varies with recirculation flow rates, which, as with the conventional HDS are controlled at approximately 25 kg of recirculated solids to each kg of new solids precipitated from the minewater (Bullen, 2006). The pH is set to optimum (~9.5) in the second reactor in order to precipitate metals of concern. Aeration is provided to first and second or at least to the second reactor for oxidation of Fe, in order to produce more chemically stable sludge (Kuyucak et al., 1995). The fully oxidised slurry is dosed with flocculant at the flocculant tank and then flows to a clarifier for liquid/solids separation. The clarifier water is discharge, whilst approximately 95% of the settled sludge is recirculated to the first reactor, with the remaining 5% of settled sludge removed from the system (Bullen, 2006).

Kostenbader et al. (1970) reported trialling the staged HDS process with little success, whereas Keefer et al. (1983) had success generating staged HDS by batch treatment trials. It was during the 1990's that the staged HDS process was originally developed by Kuyucak et al. (1995) at Noranda Technology Centre. Their patent for the process was accepted in June 1995. At the same time Unipure Environmental independently developed a type of the staged HDS process. Typical examples of the staged HDS

process can be found at Geco Mine, Ontario, Canada (Aubé et al., 1997), Wheal Jane in Cornwall, UK (Coulton et al., 2003a) and Horden, Country Durham, UK (Coulton et al., 2004).

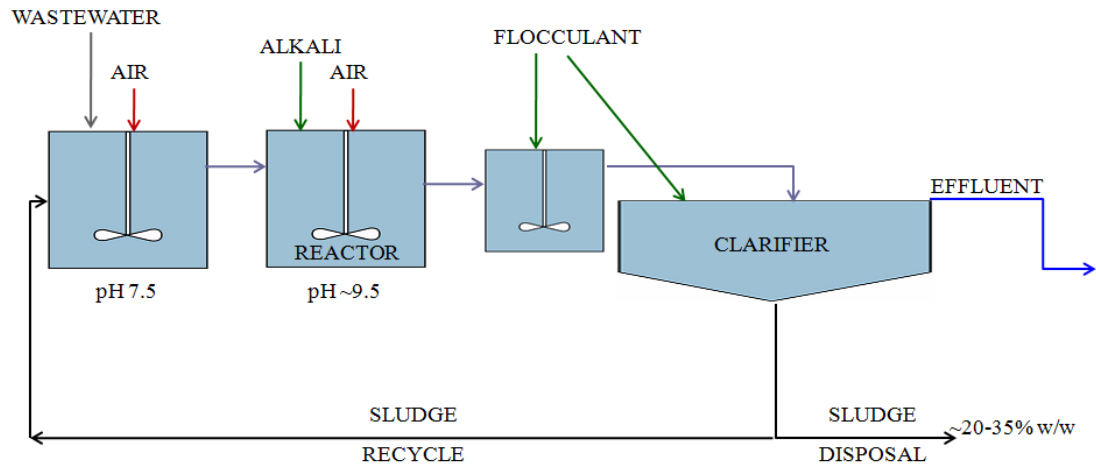


Figure 6.6 Staged HDS process

The Geco Process (Figure 6.7) uses the basic idea of staged HDS process but doesn't include a flocculant tank. Despite this, the Geco HDS process creates the densest sludge at >30% (w/v) (Aubé et al., 1997). Like with the staged HDS process, within the Geco Process, waste water and sludge are mixed in the first reactor and the sludge raises the pH of the first reactor to 7.5. Lime is added in the second reactor together with air (Aubé, 2004).

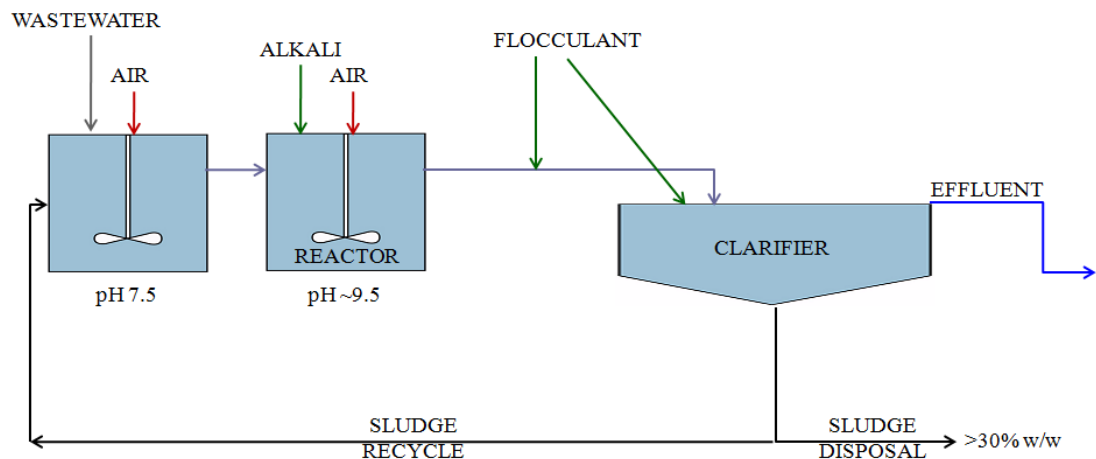


Figure 6.7 Geco HDS process (Aubé, 2004)

During the pilot plant work at the Geco mine, low initial sludge recycle ratios were in use, which resulted in the sludge not being pumpable due to the high viscosity.

However, when the sludge recycle ratios were increased, the viscosity dropped and the sludge became pumpable, resulting in recycled sludge concentrations of approximately 35% (w/v) (Bullen, 2006).

Out of the HDS processes, Geco has the lowest neutralising potential for the sludge, resulting in more lime-efficient process. Under normal conditions, this would lead to reduced long-term sludge stability, but the Geco Process was found to create a very stable precipitate (Aubé, 2004). pH increase during the Geco Process, is due to partial dissolution of the sludge and therefore reactions are occurring on the surface of the existing precipitates. The Geco process has been reported to achieve excellent results with >95% precipitation of heavy metals overall and 99% removal of Fe, Zn and Al already on the first reactor (Aubé et al. 1997).

As described above, there are a few different ways to operate a HDS process and care should be taken when choosing the right one for specific effluent treatment. Ultimately the choice between where the sludge is recycled back i.e. which type of HDS process to use is dependent on the effluent to be treated and the best high density sludge process for the treatment of a specific effluent can be only determined by pilot trials (Coulton et al., 2003b).

6.3 Formation of High Density Sludge

Kostenbader et al., (1970) developed the first high density sludge process in the 1960's at the Bethlehem Mines Corp's coal mines in Cambria, Pennsylvania U.S. in order to encourage particle growth to battle the problem of voluminous sludge.

Kostenbader et al., (1970) were unclear how the denser sludge was formed, but outlined key operating parameters that lead to the formation of HDS, including:

- Neutralisation pH,
- Point of alkalinity addition,
- Fe^{2+} to Fe^{3+} ratios in the feed water,
- Ratio of solids recirculated to new solids precipitated and
- Retention time.

While testing the Geco HDS process, Aubé et al. (1997) concluded, supporting Kostenbader et al., (1970) that it was critical to the formation of HDS sludge that neutralisation pH of the system was controlled.

The use of neutralisation and recirculation of the precipitated sludge was reported in more depth by Kuit (1980), at the Sullivan lead and zinc Mine of Cominco Ltd at Kimberley, B.C in Canada. Following considerable pilot plant work, the plant had been successfully designed to treat AMD, achieving substantially denser sludge and after approximately a year of operation, the quality of treated effluents met or even fell under the limits set for the treated effluent.

Bosman (1974) observed that iron is the main constituent of the chemical precipitate formed during AMD neutralisation. The Anglo American Research Laboratories undertook further studies on the HDS process during the early 80's and cited parameters for successful formation of HDS, including (Bosman, 1983):

- Total iron content of the acid minewater,
- Retention time in lime/sludge mix tank,
- Oxidation state of the acid minewater, i.e. ratio of Fe^{2+} to Fe^{3+} and
- Ratio of solids recirculated to solids precipitated from solution.

The parameters suggested by Kostenbader (1970) and Bosman (1983) are still reported as key to the formation of HDS process sludge (Bullen, 2006).

It is generally accepted that high iron ratios (Kostenbader et al., 1970; Bosman, 1983 and Bachon et al., 1987) or at least high overall metal concentration are required for the formation of High Density Sludge (Kuyucak, 2006; Kuyucak et al., 2001) and also using calcium-based alkali (Coulton et al., 2003b). Aubé (2005) suggest that when there is less than 100 mg/L of total metals in the incoming feed, it's difficult to attain 15% (w/v) of solids, whereas if there is a concentration of >200 mg/L Fe or Cu, more than 20% (w/w) solids are expected using the HDS process. Coulton et al. (2003b) and Bullen (2006) did however demonstrate that HDS can be formed from mine waters containing low iron concentrations and by using sodium hydroxide as the neutralising reagent.

Next to the metal concentration of the incoming feed, the sophistication of the treatment process, including the type of HDS process chosen affects the sludge solid content. Kuyucak (2006) concludes that in order to minimise the formation of a voluminous sludge, the process parameters need to be carefully considered. These include:

- Rate of neutralisation and oxidation,
- Fe^{2+} and Fe^{3+} ratio,
- Concentration of ions,
- Sludge aging,
- Recycling of settled sludge and
- Temperature and crystal formation.

Bullen (2006) carried out extensive research on how the High Density Sludge was formed. He performed a large number of batch and continuous HDS experiments and reports, contrary to previous beliefs and adding to previous knowledge that:

- HDS can be formed using non-calcium based alkali reagent, (including sodium hydroxide and carbonate),
- Iron is not required to be present in the formation of HDS,
- The Fe^{2+} and Fe^{3+} ratio in the feed water is not critical to the formation of HDS, although it does affect,
- The valence of the metals does not affect the HDS process,
- The time required for the formation of HDS and the process parameters (e.g. mass recirculation rates) depends on the characteristics of the influent feed,
- The ratio of first reactors solids to the ratio of solids formed is key to the formation of HDS and
- Surface chemistry and interactions is fundamental to the formation of HDS.

Unlike in any previous research on HDS, Bullen (2006) found that HDS with better settling and dewatering characteristics was actually formed using synthetic zinc and manganese minewater compared to synthetic iron minewater. Furthermore, he concludes that operating the first reactor at a pH in excess of the point of zero charge¹⁴

¹⁴ Point of zero charge refers to the pH at which the surface has a net neutral charge i.e. the electrical charge density on a surface is zero

appeared to enhance the formation of HDS. In a colloidal system point of zero charge exhibits what is called a zero zeta¹⁵ potential.

6.3.1 Development of the HDS Process

In recent years, the research looking into the formation of HDS has concentrated more on understanding how the sludge with high densities is formed. Some of this work has concentrated on nucleation and crystal formation (Stumm et al., 1996; Dempsey, 1993) and has concluded that during HDS process, the nucleation or precipitation of metals is able to take place on a solids surface (heterogeneous) or in a solution (homogeneous). The location of nucleation can be controlled by the level of supersaturation¹⁶ (Bullen, 2006). Supersaturated conditions can be relieved by one of two ways. Solute can either form new particles (nuclei) or deposit itself onto existing surfaces (Mullin, 1997). More information on crystal growth and nucleation is available in literature (Stumm et al., 1996; Mullin, 1997 and Bullen, 2006).

Dempsey (1993) investigated how the control of nucleation/crystal growth rates affected the production of HDS sludges. Bench scale tests were carried out using synthetic solutions using different processes and mechanisms. These included:

- Conventional HDS process,
- Manipulation of the zeta potential during the precipitation of Fe^{3+} hydroxide,
- Minimising supersaturation rates and
- Physical/chemical disruptions to convert low density sludge into HDS sludge.

Dempsey (1993) suggested that by controlling the degree of supersaturation the new precipitates do not form as new primary particles, but heteronucleation or crystal growth occurs, resulting in high density sludge formation. This process can be controlled by managing the circulation rates, as crystal growth is proportional to the solids surface area (Bullen, 2006). Using the above principles, Dempsey (1993) reported a fourfold increase in the density of the sludge by controlling the pH and the zeta potential.

¹⁵ Zeta potential refers to electrokinetic potential in colloidal systems. Lower the potential, lower the electric stability and higher the coagulation/flocculation rate of the particles

¹⁶ Supersaturation refers to a solution that contains more dissolved material than could be dissolved under normal circumstances

The Staged-Neutralization (S-N) process (Aubé, 2004) applies crystallisation principles in order to both enhance sludge crystallinity and reduce sludge volume (Demopoulos, 1995). As seen in Figure 6.8, the Staged-Neutralization process involved neutralising the effluent in a series of steps to control the level of supersaturation during metal precipitation (Aubé, 2004). The process uses recycled sludge in the first two reactors to partially neutralise the incoming effluent. The sludge is used to control the pH. Within the third and the fourth reactor, lime slurry is used to bring the slurry to a desired pH. The four precipitation reactors are followed by a flocculant reactor and a clarifier.

This process has been patented in the both the U.S. and Canada (Demopoulos et al., 1997; Zinck et al., 2001), but it is yet to be applied in a full scale (Aubé, 2004). Despite of the excellent sludge properties and low lime consumption that are to be expected (Aubé, 2004), the capital expenditure would be very high due to the amount of reactors required.

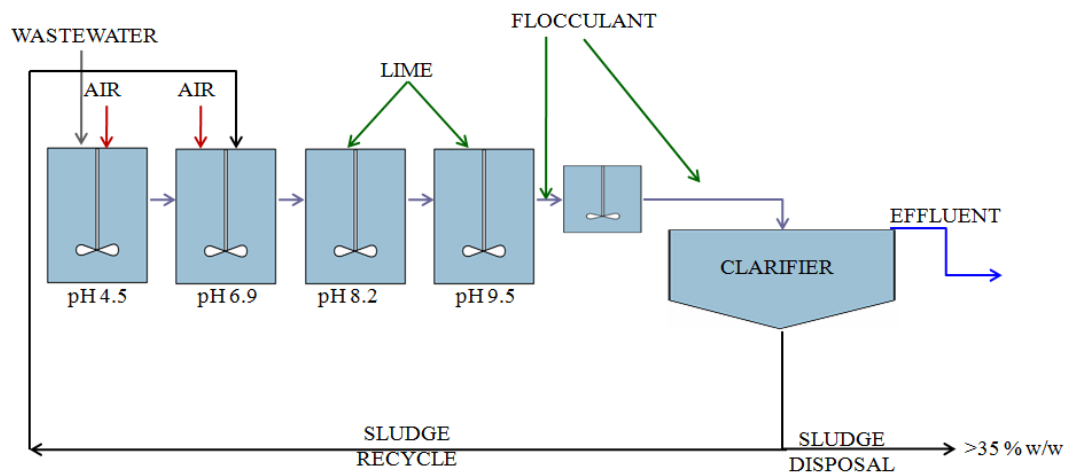


Figure 6.8 Staged-Neutralization process (Demopoulos et al., 1995)

6.4 Important Process Parametres for the Formation of HDS

There are many parametres that are important for the formation of HDS and that will affect the quality of the formed HDS. Based on the current knowledge, the most important process parametres for the formation of HDS include:

- Neutralisation pH,
- Point of alkalinity addition,
- Retention time and

- Ratio of solids recirculated to new solids precipitated.

Against the common belief, Bullen (2006) reported that when it comes to solid recirculation, it is the ratio of first reactors solids to the ratio of solids formed that is key to the formation of HDS.

6.4.1 Solid Recirculation Ratio

HDS process is distinguished from the conventional precipitation system by the solid recirculation that is imperative for the creation of HDS.

The solid recirculation ratio is often measured as:

$$\frac{\text{(mass of solids recycled per unit time)}}{\text{(mass of solids formed per unit time)}}$$

I.e. on a weight by weight basis

Several different values are given for the sludge recirculation ratio throughout the literature and the choice of the ratio appears to relate to both the HDS process technique used as well as to the type of effluent water to be treated.

When running a conventional HDS treatment plant at Heath Steele to treat pickle liquor, Kostenbader (1971) reported a recirculation rate of 20:1. Sengupta (1993) reported 20:1 to 30:1 as the optimum ratio of solids recirculation using conventional HDS treatment for AMD.

Aubé et al. (1999) considered the recirculation rates during both conventional and staged HDS processes while treating AMD and indicated that best recycling ratio would be between 10:1 and 30:1, resulting in 90% of the solids being in the lime reactor at any given time. Later on Aubé (2005) suggested that recirculation ratio between 20:1 and 25:1 works best when treating AMD by a HDS process.

Following pilot testing findings, with an AMD-mimicking synthetic feed, the recycle ratio was found to be best between 20:1 and 45:1 (Canadian Environmental & Metallurgical Inc., 2002).

When treating AMD at the Wheal Jane mine using staged HDS, Coulton et al (2003a) reported recirculation between 25:1 and 50:1. While Bullen (2006) was running several continuous staged or Type II HDS pilot plant trials, the maximum settled sludge densities were achieved at a recirculation ratio of between 25:1 and 30:1. Furthermore, Bullen (2006) concluded that when high concentrations of other ions are present, including chloride, calcium and magnesium, higher recirculation ratios are required.

6.5 Sludge Quality

Sludge produced by conventional chemical precipitation is voluminous in nature with solids concentrations for settled sludge ranging from 1 up to 5% of solids (w/v) (Kuyucak, 2006; Dempsey et al., 2001; Ming et al., 2009) and further dewatering can be problematic (Dempsey et al., 2001). Voluminous sludge is born when the electrostatic (zeta) potential causes the sludge particles to repel each other.

Despite the improvement to the conventional neutralisation method (Kuit, 1980; Vachon et al., 1987; Kuyucak et al., 1991; Demopoulos et al., 1995; Aubé, 1999), the sludge quality created by conventional precipitation remains poor. In Canada alone, it is estimated that 6.7 million cubic metres of lime treatment sludge is produced annually (Zinc, et al 1997) and this rate is expected to increase (Zinck, 2005). In some cases the volume of sludge produced can approach the volume of the original effluent treated (Murdock et al., 1995).

The use of the HDS process greatly affects the characteristics of the sludge generated. The sludge characteristics have been widely studied and reported in the literature. Sludge densities were reported by Kostenbader et al., (1970); Bosman, (1983); Zinck, (1997); Aubé et al., (1999), the particle size, sludge composition and mineralogy and morphology by Zinck, (1997); Aubé et al., (1999) and dewaterability of the sludge by Kuyucak (2001); Zinck et al. (2001).

As explained previously, the sludge recycling used in the HDS process encourages nucleation, with the metals in the incoming effluent stream precipitating on the surface of previously created sludge particles. This leads to particles growing to approximately

3 to 12 microns in diameters (Coulton et al. 2003a). Aubé et al. (1999) reported that sludges produced by HDS display both smaller median particle sizes and narrower particle size distributions.

Another challenge faced by the acid mine drainage treatment is long-term chemical stability of the sludge and it has been reported that the use of a conventional precipitation systems using lime leads to creation of unstable secondary sludges (Kalin et al., 2005). The HDS process creates more stable sludges and it has been reported that the geochemical stability of the precipitates is even more favourable when there's a high iron to total metal ration in the plant feed (Canadian Environmental & Metallurgical Inc., 2002). The chemical stability of the sludge can be quantified by leaching studies that have been conducted by several researchers looking into HDS over time. Chemical stability is however not as important with the sludge arisen following final effluent treatment at steelworks due to the nature and concentrations of the metals and other constituents present in the treated effluent.

6.5.1 Sludge Densities during HDS

Achieving as high as possible sludge density is the main purpose of the HDS process and the literature outlines a huge variation in the sludge densities achieved by using or experimenting with HDS processes.

Using optimum operating parametres, Kostenbader, et al., (1970) reported that conventional HDS was forming between 15% (w/v) and 35% (w/v) of solids. During conventional HDS experiments Bosman (1974) was able to achieve sludge densities between 11.5 and 23% (w/v). Aubé et al. (2001) reported concentrations of 32.8% (w/v) using the Brunswick conventional HDS process plant. Demopoulos et al. (1995) reported solids concentration of 55% (w/v) using NaOH as an alkali reagent and 67% (w/v) sludge solids concentrations using lime as the alkali reagent during staged-neutralisation experiments. Zinck et al. (2001) undertook pilot plant trials to compare the various forms of the HDS process and reported 23.3% (w/v) sludge densities by using staged-neutralisation process and staged HDS process and 13.9% (w/v) sludge densities by using Geco process.

Coulton et al. (2003a) concluded that HDS typically allows sludge concentrations of 15 to 25% (w/w) at the thickener and following the clarification/thickening 50 to 80% (w/w). While operating Wheal Jane mine staged HDS plant Coulton et al. (2003a) achieved sludge with a density of 20% (w/w).

According to Kalin et al. (2005) the HDS plants can achieve sludge densities of 30% (w/v) or better, while Kuyucak (2006) concludes that HDS process results in solids content between 10-30% (w/v).

6.6 Advantages of HDS

During the 1960's and early 1970's the HDS process was developed as a means of producing sludge with higher settled solid concentrations. The solid concentration of the HDS aside, there are many advantages in using a HDS process instead of a conventional precipitation system. According to Dey, et al. (2007), the characteristics of HDS process not only enhance the removal efficiency of the effluent treatment process, but also provide a superior sludge in terms of handle-ability and disposal.

One of the biggest advantages is that the HDS process is reported to improve the sludge settling and dewatering characteristics (Zinc et al., 2000; Aubé et al., 1997; Bosman, 1983; Bullen 2006). This is due to the density and the volume of the particle changing in line with the Equation 6.1 that governs particle settling as outlined by the Nalco Chemical Company (1988):

$$F \propto g \frac{(S_1 - S_2)}{V} \quad (\text{Equation 6.1})$$

where:

F = impelling force

g = gravitational constant

V = volume of the particle

S₁ = density of the particle

S₂ = density of the fluid

Bullen (2006) recorded settlement velocities of 18 m/hr for staged HDS, whereas the experiments carried out by the author as a part of the present research study found that sludges produced via conventional precipitation have settlement velocities of approximately 10 m/h and matured staged HDS process sludges up to 25 m/hr. Coulton et al (2003a) states that HDS settles at significantly greater velocities and can be easier thickened than conventional hydroxide precipitates. This results in reduction in the size of the solid/liquid separation unit. According to Coulton et al (2003a), at the Wheal Jane Minewater Treatment Plant, the use of HDS process together with a lamella clarifier has allowed the solid/liquid separation unit to be reduced to about 13% of the original used during conventional hydroxide treatment system. Bullen (2006) states that the reduction of the sludge volume produced by HDS process can reduce the operational costs of the treatment plant substantially.

Keefer et al. (1983) were researching the conversion of minewater treatment sludge into a coagulant in batch treatment trials, when they had a success in generating staged HDS. The trials indicated that a lime saving of >31% was achieved in comparison to conventional precipitation. Aubé (2004) reports increased lime efficiency due to HDS process promoting dissolution of unused reagent through repeated contact with the wastewater and Ming et al., (2009) concludes that consumption of lime reduced by 33.3% by using HDS process.

Aubé (2004) found HDS process to reduce scaling on the reactor walls and conduits to the clarifier. However, with wastewater containing high sulphate concentrations, gypsum scaling can occur following the addition of Ca from lime. Furthermore, if the pH setpoint is high (for treating Ni or Cd) calcium carbonate (calcite) scaling can occur. Fortunately in the HDS systems, the precipitation of gypsum or calcite occurs on the surface of existing particles instead of reactor surfaces (Aubé, 2004). The reduced scaling is due to the calcium and sulphate ions attaching themselves into the charged sludge particles, instead of forming gypsum and causing scaling of the walls of the equipment and piping as seen in Figures 6.9a and 6.9b.

One disadvantage of the HDS process is that the Lime/Sludge mixture can be very viscous and causes a soft scaling which can clog up the reactor. This leads to reduced

retention time of the lime/sludge mixing tank and can cause the overflow to be plugged up (Aubé, 2004).

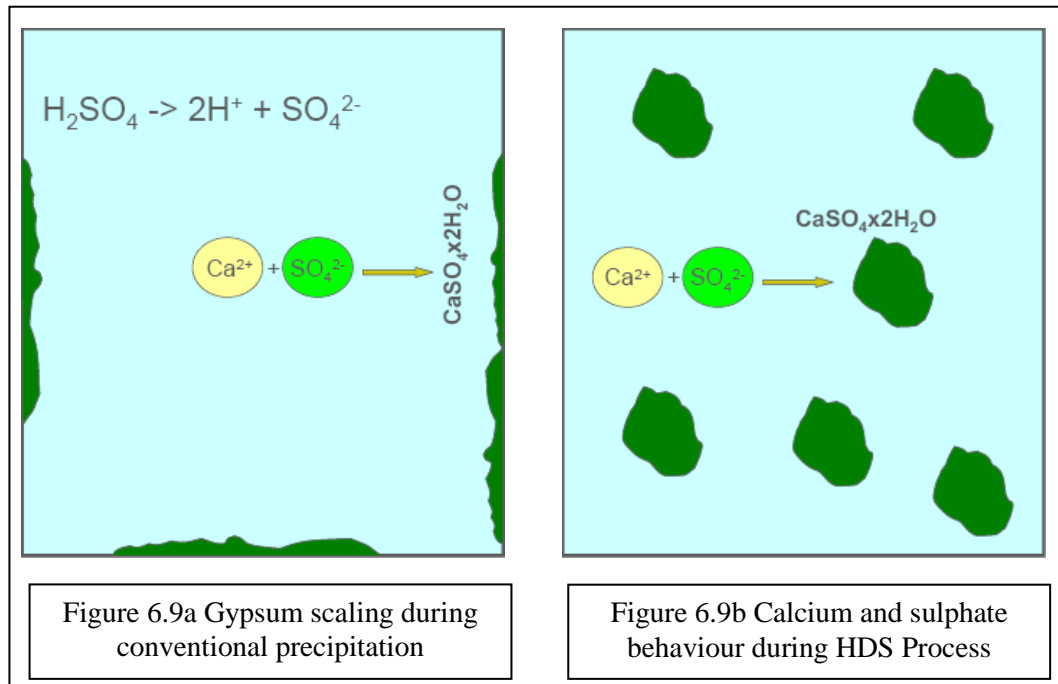


Figure 6.9 Scaling behaviour during conventional precipitation and HDS process

6.6.1 Sludge Disposal

Haines et al. (1968) indicated that conventional lime precipitation of Pickle Liquor effluent at Heath Steel can only achieve sludge densities of only 1% (w/v). Measurements of sludge densities arisen at the Port Talbot Steelworks current final effluent treatment system, using conventional precipitation with sodium hydroxide, give very similar results of just under 1% (w/v). Further dewatering of conventional precipitation sludge can be problematic (Dempsey et al., 2001), even when using mechanical filter pressing equipment, such as filter presses or similar.

Cox et al. (2006) concluded that the reduced sludge volume and improved sludge quality by using HDS process can lead to 50% cost savings on sludge handling and disposal (Cox, et al., 2006)

6.7 Sludge Dewatering

The sludge arising from effluent treatment requires safe disposal. The cost of sludge disposal within the metal industry depends on several things, including:

- Volume of sludge
- Nature of the sludge (toxicity and leachability)
- Transportation requirements and
- Landfilling options.

Volume of sludge is nevertheless by far the most important factor in the overall cost of the disposal and hence sludge dewatering plays an important role in reducing the costs related to sludge management. Cox et al. (2006) states that HDS in itself can lead to 50% cost savings on sludge handling and disposal. This is due to the reduced volume of sludge and improved dewatering characteristics (Dey et al., 2007), further dewatering of sludge arisen during conventional precipitation can be problematic (Dempsey et al., 2001).

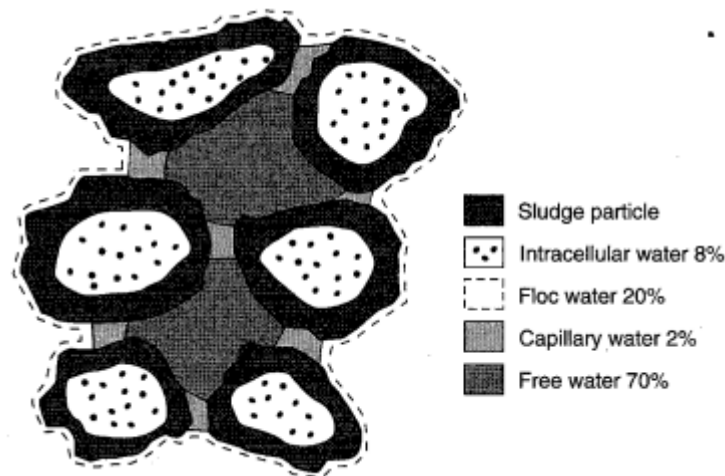


Figure 6.10 Schematic diagram of a sludge floc showing the association of the sludge particle with the available water (Gray, 2005 – Reproduced from Best, 1980)

According to Gray (2005) at moisture contents $>90\%$, sludges behave as liquids while at $<90\%$ moisture content they are behaving as non-Newtonian fluids with non-viscous flow. In the sludges with a moisture content of $>95\%$ the water is in a free form (Figure 6.10), while the remainder is bound to the sludge and is more difficult to remove, requiring mechanical dewatering.

The liquid/solids separation is important for sludge volume reduction that results in cost savings, but also, especially at regions of water scarcity for retaining freshwater that would otherwise be disposed together with the sludge.

Several different mechanical sludge dewatering technologies are available, while the most commonly used in Europe include: filter and belt presses, vacuum filtration and centrifugation. The mechanical sludge dewatering techniques are often used as they aid with the liquid/solid separation by altering the particle formation of flocs and the cohesive forces that bind the particles together, thus releasing floc and capillary water (Gray, 2005).

6.7.1 Filter Pressing

Filter presses are commonly employed in the metal and mining industry to enhance the liquid/solid separation. Since 2008, there has also been a filter press in use for the final effluent treatment sludge dewatering at the Port Talbot Steelworks, which is to be expected when using sodium hydroxide, which according to Kuyucak (2006) results in sludge that does not settle well and requires filtering in most cases.

Produced in 1950's, the filter presses are amongst the oldest mechanical dewatering devices around (BHS Filtration, 2008). The operation of a filter press happens in batches and it is based on using pressure to push the sludge through a filter cloth. The filter presses are often divided into over-pressure filters or under-pressure filters depending on how the pressure is applied. The product remaining after the sludge dewatering is called filter cake.

According to Vasilind (2003) the primary advantage of a filter press system is that it often produces cakes that are drier than those produced by other dewatering alternatives. Filter presses have adaptable operation to a wide range of solid characteristics, acceptable mechanical reliability, comparable energy requirements to other dewatering systems and a high filtrate quality. The significant disadvantages of filter presses are their high capital cost and relatively high operating and maintenance costs.

6.7.2 Sludge Filterability

In assessing the filterability of sludge it is necessary to consider not only the resistance to filtrate flow offered by the cake (measured by its specific resistance in m/kg) but also the cloth resistance which is a function of the type of cake produced. As described in Section 6.6 of this chapter, there is an extensive difference between the filterability of HDS process and conventional precipitation sludges.

6.7.2.1 Specific Resistance to Filtration and Cloth Resistance

The sludge filterability measurement is based on the concept of flow through a porous medium (Mininni, et al., 1984) and the unit of measure used is called specific resistance (m/kg) to filtration (Christensen, 1983), which might be defined as the resistance of sludge, having a unit weight of dry solids per unit area at a given pressure, to a unit rate of flow of liquid having unit viscosity (Berkday, 1998).

The specific resistance of sludge to filtration (Equation 6.2) can be calculated using the following equation (Christensen, 1983):

$$r = \frac{2bPA^2}{\mu c} \quad (\text{Equation 6.2})$$

where:

r = specific resistance (m/kg),

b = slope of the time/volume versus volume plot (Sec S/m³/m³),

P = pressure drop across the sludge cake (Pa),

A = filtration area (m²),

μ = viscosity of filtrate (Pa S) and

c = dry cake mass per unit volume of filtrate (kg/m³).

The higher the value of specific resistance indicates a sludge which is more difficult to dewater, whereas with lower values of specific resistance, no further conditioning of sludge is required.

Laboratory filtration experiments make it possible to determine the specific resistance to filtration (r) and cloth resistance by plotting the ratio of time to volume (t/V) of the filtrate as a function of volume (V) (Equation 6.3). Using this method, the rate of filtration of sludge is given by (Coulson, et al., 1991):

$$\frac{t}{V} = \frac{r \mu c V}{2A^2 \Delta P} + \frac{\mu R_m}{A \Delta P} \quad (\text{Equation 6.3})$$

where:

t = time in seconds (s),

V = filtrate volume obtained after time t (m^3),

r = specific cake resistance (m/kg),

ΔP = pressure drop across the sludge cake (Pa),

A = filtration area (0.0045) (m^2),

μ = viscosity of filtrate (0.001) (Pa s),

c = dry cake mass per unit volume of filtrate (kg/m^3) and

R_m = resistance of the filtration medium (Cloth resistance) (m^1).

For a constant pressure with an incompressible cake, there is a linear relationship between t/V and V . The slope of the line, a , and the intercept, b , are defined as (Equation 6.4 and 6.5):

$$a = \frac{r \mu c}{2A^2 \Delta P} \quad (\text{Equation 6.4})$$

$$b = \frac{r \mu c R_m}{2A^2 \Delta P} \quad (\text{Equation 6.5})$$

The slope of the line and point of interception can be calculating by plotting the graph t/V against V . The specific cake resistance and the cloth resistance can furthermore be calculated by using the slope of the line and point of interception.

6.8 Laboratory Studies – Continuous High Density Sludge Process Trial for Steelworks Final Effluent

In order to investigate options for sludge reduction in the present study, a High Density Sludge (HDS) process was operated in pilot scale using chemical feed stock imitating

Steelworks final effluent. HDS was achieved by mixing recirculating sludge and the feed water prior to adding the alkali, creating a so-called staged (Kuyucak et al., 1995) or HDS II process (Bullen, 2006), where recirculated sludge acts as a seed for further metals precipitation. A total metal feed concentration of under 100 mg/L and zinc metal concentrations under 50 mg/L was used based on the analysis of Port Talbot Steelworks final effluent.

The trial was used to test if HDS could be formed using:

- Non-acidic feed,
- Non iron-containing feed,
- Feed with low metal concentrations and
- Sodium hydroxide as an alkali reagent.

The objectives of the continuous trial were to:

- Successfully operate a staged HDS process laboratory pilot plant to generate staged/Type II HDS from a synthetic feed mimicking steelworks final effluent,
- Examine the efficiency of HDS in treating a synthetic feed mimicking steelworks final effluent and reagent use and creating HDS with suitable densities,
- Examine suitability of the staged HDS process in creating relevant sludge densities and settlement characteristics from synthetic feed mimicking steelworks final effluent,
- Demonstrate that Type II HDS can be formed using sodium hydroxide (NaOH) as a reagent,
- Demonstrate that Type II HDS can be formed by using non-acidic feed and
- Demonstrate that Type II HDS can be formed by non-iron containing or very low iron concentration feed water.

A continuous trial with a HDS process pilot plant was carried out during the two months leading up to 16.02.2010 in order to confirm that HDS could be produced using sodium hydroxide as the alkali reagent. Zn, Cu, Fe, Ni and Mn were added to Cardiff tap water to give the desired concentrations. The tap water was dosed with the appropriate amounts of Mg and Ca to mimic the background concentrations found at the steelworks.

6.8.1 Plant Description

A photograph of the pilot plant can be seen in Figure 6.11 and a more specific process flow diagramme is presented in Figure 6.12.

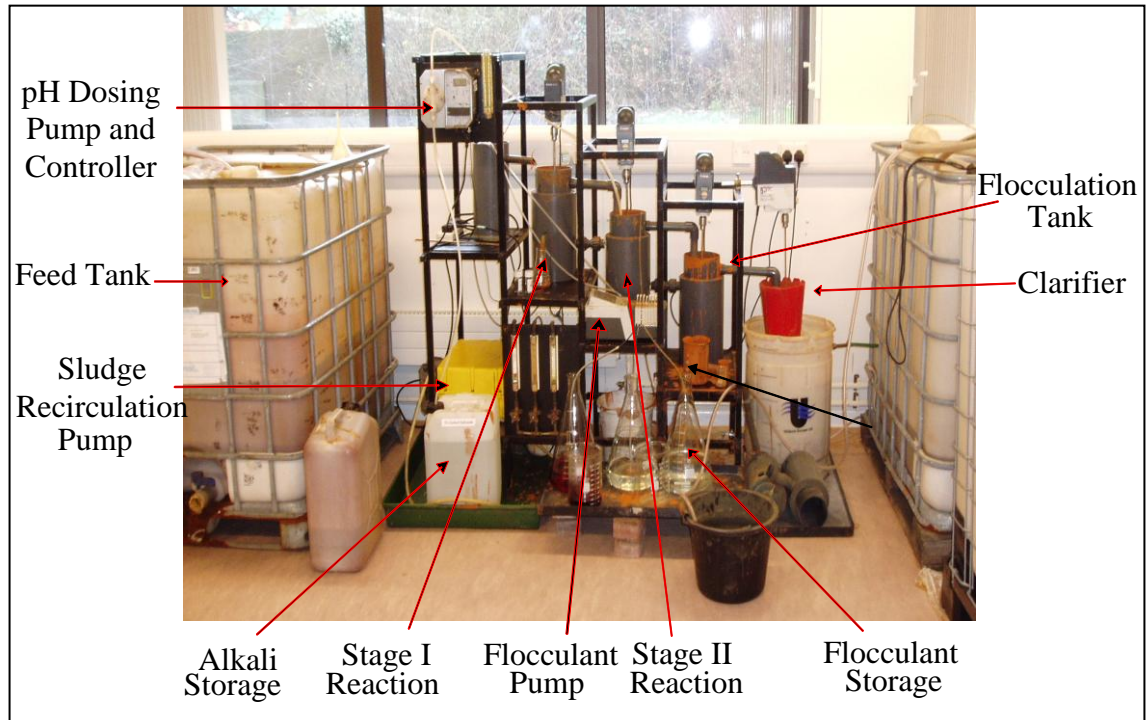


Figure 6.11 Photograph of the HDS process pilot plant (Suvio et al., 2010b)

The pilot plant consists of an influent water storage tank and a feed pump, Stage I Reactor tank, Stage II Reactor tank, flocculation tank and a clarifier. Ancillary equipment includes alkali reagent (sodium hydroxide) and anionic flocculant and their storage and dosing systems as well as air supply (for metal oxidation). A flow rate of 10 litres / hour was chosen, giving a nominal flow with 30 minute retention time in the first two 5 litre reaction tanks.

Within the pilot plant, the HDS was achieved by mixing recirculating sludge and the feed water prior to adding the alkali, creating a so-called staged (Kuyucak et al., 1995) or HDS II process (Bullen, 2006), where recirculated sludge acts as a seed for further metals precipitation and alkali is only added at the second (Stage II) reactor as explained in more detail in Section 6.2.3.3 of this chapter.

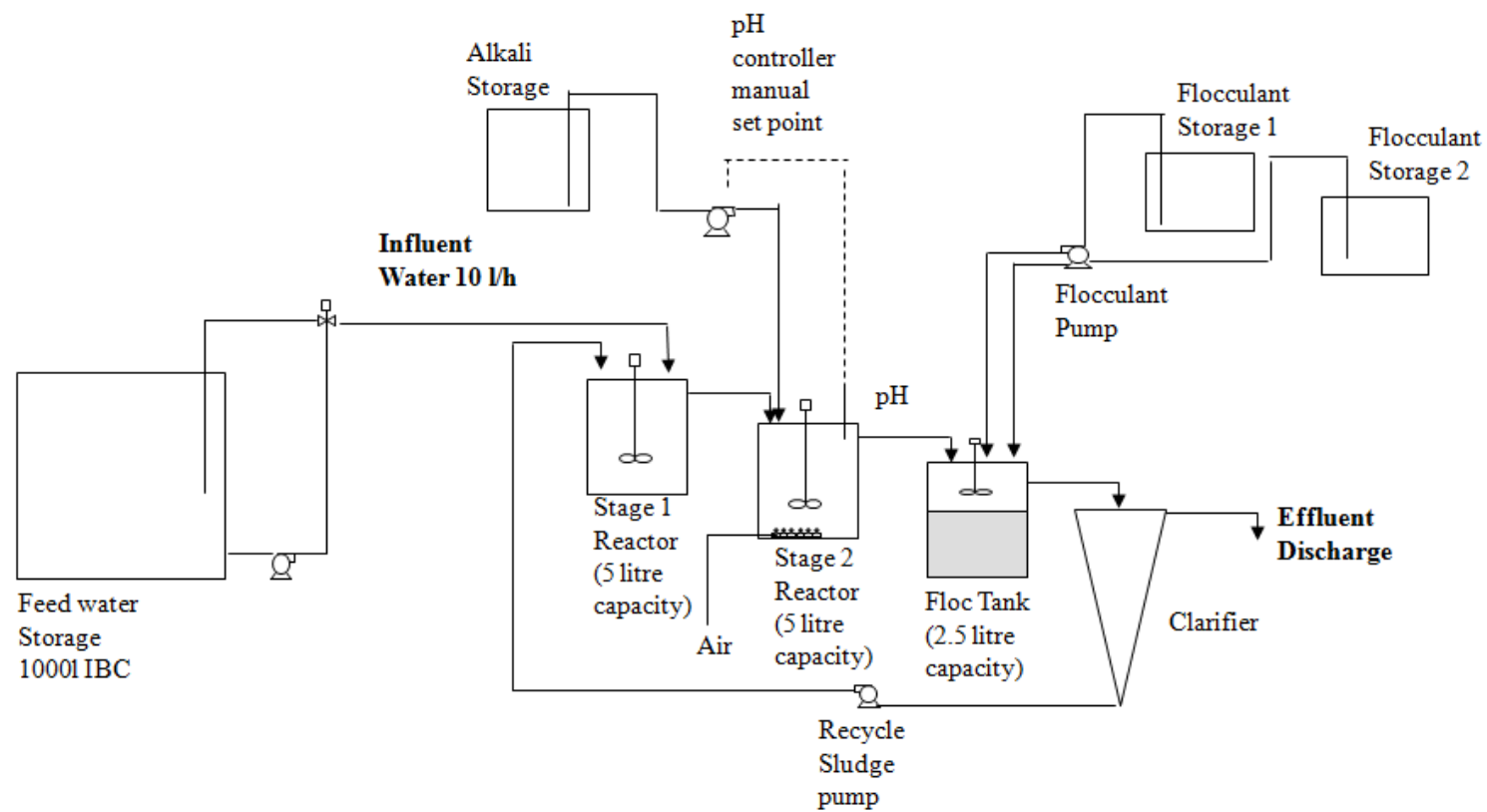


Figure 6.12 Process flow diagramme of the HDS process pilot plant

A brief description of each stage of the pilot plant follows.

6.8.1.1 Influent Water Preparation, Storage and Pumping

The first stage of the plant consists of a 1 m³ Intermediate Bulk Container (IBC) influent feed water storage tank. The chemical composition of the water in the IBC was achieved by adding relevant chemicals to tap water to simulate Port Talbot Steelworks final effluent characteristics.

The content of the IBC was manually stirred daily to ensure the contents were fully mixed. A peristaltic feed pump (Watson Marlow SciQ 323) was used, aiming for a nominal incoming feed flow rate of 10 L/h (30 minute retention time in each of the first two reactors).

6.8.1.2 Stage I Reactor Vessel

The plant feed was mixed with the recycled sludge in the 5-litre Stage I reaction tank (cylindrical with a radius of 0.075 m and a height of 0.28 m). A top mounted mixer (a Heidolph RZR 2041 operated at speed setting 1 at 302 rpm) was installed in the Stage I reactor to keep the solids in suspension. The sludge was used to raise the pH of the reactor.

6.8.1.3 Stage II Reactor Vessel

The overflow from the Stage I reactor was fed into the similarly sized Stage II reactor, where the pH was raised by the addition of alkali (NaOH). The aim was to keep the pH of the reactor around 8.5, which is an ideal pH for the removal of zinc as described in Chapter 5. Air was introduced to the Reactor via a diffuser ring at a rate of 10 L/h to ensure the full oxidation of the metals. A top mounted mixer (a Heidolph RZR 2041 operated on speed setting 1 at 200 rpm) was used to ensure adequate mixing.

6.8.1.4 Alkali Reagent Dosing System

The alkali was stored in a 25 L storage vessel and the stock solution was made up to a strength of 5% by dissolving 50 g of sodium hydroxide pellets per 1 litre of hot tap water, which ensured that all the pellets dissolved. The sodium hydroxide was stored in a 25 litre vessel and each day the volume of the alkali added was recorded. The sodium hydroxide was supplied from a storage vessel and dosed to the Stage II reactor via an integral controller/metering pump (Hanna Instruments BL 7916). A pH controller was used to maintain the Stage II Reactor pH appropriate for the metals in the influent feed water. The alkali dosing rate was controlled via a pH probe located at the outlet of the Stage II reactor. The pH controller was calibrated three times a week and the pH measurement was also double-checked using a Hanna Instruments HI208 portable pH meter. Both of the pH meters were calibrated to an accuracy of 0.2 pH.

6.8.1.5 Flocculant Make-up System

Anionic flocculant (Superfloc A-110 by Kemira Oyj) was made up at a concentration of 0.05% (i.e. 0.5 g of active flocculant/L). The flow of flocculant was set so that a dose of approximately 2.5 mg/L would be achieved. The dosing pump used was a FA Hughes (DCL) peristaltic pump. In order to guarantee pumping reliability in such low volumes of flocculant, two pumps were used. Therefore, should one pump fail, the flocculant dosing system would not totally fail. The volume of flocculant added was logged on a regular basis and additional “drop” tests were carried out regularly to ensure correct dosage rate.

6.8.1.6 Air Blower System

Air was supplied to the Stage II Reactor for metal oxidation. The air was introduced via a diffuser ring located at the bottom of the Reactor. The airflow was initially set at approximately 5 L/min, but due to the small amount of metals requiring oxidation present in the influent feed, the rate was not recorded during the trials. The flow rate was however checked weekly. A top mounted mixer (a Heidolph RZR 2041 operated on speed setting 1 at 200 rpm) was used to increase oxygen transfer.

6.8.1.7 Flocculation Tank

The treated water from the Stage II reactor overflowed into the flocculant tank (volume 2.5 L, cylindrical with a radius of 0.075 m and a height of 0.14 m). Flocculant was added to the feed line from the Stage II reactor. A slow-speed flocculation mixer (a Heidolph RZR 2041 operated on speed setting 1 at 141 rpm) was used for solids and flocculant mixing. The flocculated mixture then flowed via gravity into the clarifier.

6.8.1.8 Clarifier/Thickener Unit

Solids/liquid separation was achieved in a clarifier/thickener cone, with a maximum surface area of approximately 0.0176 m². A slow-speed mixer (a Heidolph RZR 2041 operated on speed setting 1 at 70 rpm) was used to assist solids/liquid separation. Treated water was discharged from the system by overflowing the clarifier unit.

6.8.2 Sludge Recirculation

Thickened solids from the clarifier were recirculated to the Stage I reactor by peristaltic Watson Marlow 604U pump. No solids were purposely removed from the system during the trial.

6.9 Laboratory Studies – Filtration Experiments

In order to determine how the filtration characteristics of the sludge changed during the HDS process experiment and how these filtration results compare with conventional precipitation (Chapter 5) sludge filtration results, piston press tests were undertaken on sludge samples.

6.9.1 Svedala Piston Press Description

The filtration experiments were carried out using a Svedala piston press that was borrowed from Silbuster Solutions Ltd in Monmouth, UK. A schematic representation of all the components and operational positioning of the piston press can be seen in

Figure 6.13. Figure 6.14 outlines photographs of each major component of the Svedala piston press and a photograph of the piston press in operation.

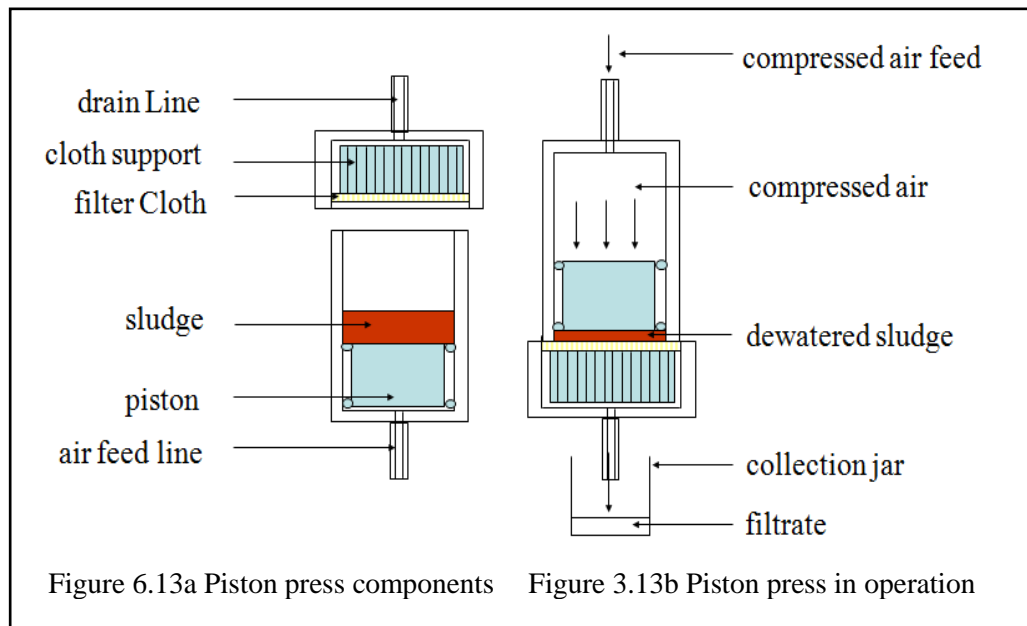


Figure 6.13 Schematic diagram of the Svedala piston press (Bullen, 2006)

6.9.2 Filtration Experiment Procedure

During the experiments, the piston press was inverted (Figure 6.13) and the piston itself was gently dropped inside the cylinder, which had a 1-litre volume and a diameter of 0.076 metres. In order to produce an air tight seal an 'O'-ring was used between the piston and sludge sample in order to produce an air tight seal. During the experiments, a sludge sample of volume (0.5 litres) and known concentration was introduced on the top of the piston.

The media or 'filter cloth', which was a fine cotton cloth, was then placed on the cloth support and the cloth support was placed into the end cap. During the first experiments it was noted that water leaked from between the filter cloth and the filter cloth support and therefore an additional 'O'-ring (O-shaped rubber ring with approximately 0.5 cm thickness) was added between the filter cloths and the filter cloths support. The assembled press was then inverted and locked in a vertical position and a measuring cylinder was placed under the piston in order to capture the filtrate. Compressed air was then applied to the unit using a pressure of 5 bars, while the volume of the filtrate was

recorded every 5 seconds. Furthermore to the volumes recorded at regular intervals, an additional volume was recorder at the end of the test at ‘breakthrough’. Following the filtration test, the filter cake solid concentration % (w/w) was measured using the ‘Total Suspended Solids Methodology’ described later on in Section 6.10.1.1 of this chapter.



Figure 6.14a: Photograph of the piston press filter cloth support



Figure 6.14b: Photograph of the piston press end cap and piston



Figure 6.14c: Photograph of the piston press cylinder



Figure 6.14d: Photograph of the piston press in operation

Figure 6.14 Photographs of the Svedala piston press

6.10 Water Analysis Techniques

Throughout the pilot plant experiments, water and sludge samples were taken at regular intervals. The continuous pilot plant was located within the Cardiff University CLEER

(Characterisation Laboratories for Environmental Engineering Research) facility and the analysis of the samples was carried out within the same Laboratory. A few individual methodologies were used to analyse the samples as outlined below.

6.10.1.1 Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry Metal Analysis

Daily samples were taken throughout the pilot plant for the analysis of dissolved metal concentrations. Prior to the analysis, the samples were filtered through a 0.2 µm filter in order to remove any settleable solids, including insoluble metals and suspended solids.

The elemental analyses of metals was undertaken by a Cardiff University CLEER Laboratory Technician, Mr Jeff Rowlands, using Perkin Elmer Optima 2100 DV ICP-OES Inductively Coupled Plasma Optical Emission Spectroscopy.

Prior to the analysis, the ICP was calibrated by Mr Rowlands for the relevant element to be analysed, therefore ensuring consistent accuracy. The calibration was done by using standard samples, which were run through the ICP at the start of the each analysis. The analysis was undertaken by file method. Detection limit for the Perkin Elmer ICP-OES devices for relevant elements are shown in Table 6.1.

The method for using ICP metal analysis is outlined in several water and wastewater analysis books, including the ‘Standard Methods for the Examination of Water and Wastewater’, Part 3120 B.

Table 6.1 Detection limits for Perkin Elmer ICP-OES devices (Perkin Elmer, 2008)

Element	Detection limit (µg/L)
Zn	0.2
Ni	0.5
Pb	1
Cr	0.2
Cd	0.1
Mn	0.1
Mg	0.04

It should be noted however that in laboratory environment it is common to only achieve mg/L values as detection limits, despite the potential detection limits of the relevant Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry device.

6.10.1.2 Total Suspended Solids Methodology

In order to determine the total suspended solids concentration the sample was filtered using a filter funnel and the sludge together with the filter paper was placed in an oven at a temperature of approximately 105°C for a minimum of 2 hours. The amount of total suspended solids in the sample was attained by measuring the difference in weight between the filter paper prior to the filtering and the weight of the filter paper and dried solids following the oven treatment.

The full procedure and methodology is presented in the ‘Standard Methods for the Examination of Water and Wastewater’, Part 2540 C.

6.11 Results

Several results can be derived from the HDS process pilot plant experiment, which include pilot plant performance monitoring results, including: water treatment efficiency, pH's throughout the pilot plant, reagent consumption, sludge recirculation ratio and sludge densities. Furthermore results on sludge settlement characteristics were derived from the HDS process pilot plant experiment.

The specific resistance to filtration and cloth resistance results were derived from the results of the sludge filtration experiments carried out using HDS process experiment sludges as well as conventional precipitation sludge.

6.11.1 Pilot Plant Performance Monitoring

The performance of the pilot plant was assessed by monitoring several aspects during the trial. The monitoring included daily checks of volume of feed water, reagent

consumption (volumes of added flocculant and alkali), as well as the pH's and water quality throughout the plant. The volume of sludge returned to the Stage I reactor was regularly monitored in order to determine correct recirculation ratio, sludge settling velocity tests were carried out using sludge from the flocculant tank from which also the sludge density was determined. Finally, samples were taken from the clarifier to determine achieved sludge density at regular intervals during the trial.

Analysis of the pilot plant performance monitoring results follows.

6.11.1.1 Plant Flows and Reactor Retention Times

A flow rate of 10 litres / hour was chosen, giving a nominal flow with 30 minute retention time in each of the first two 5 litre reaction tanks. The volume added to the pilot plant was logged daily by measuring the volume of influent feed used from the IBC. Additionally daily “drop” or flow calibration tests measuring times required to deliver known volumes into measuring cylinders were carried out to ensure the correct water feed rate was obtained.

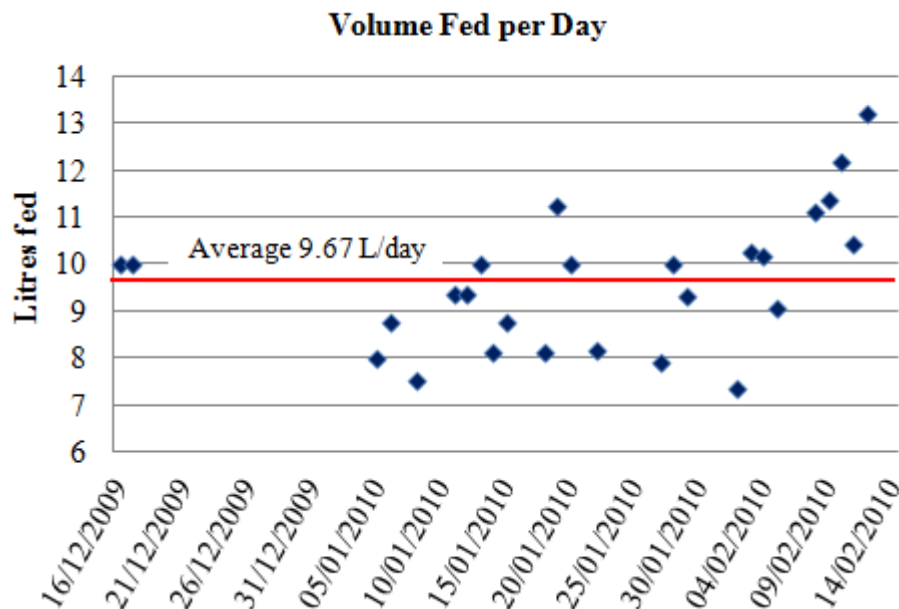


Figure 6.15 Average L/hr influent feed volume during the pilot plant trial

The actual volume fed daily can be seen in Figure 6.15, from which it can be seen that during the experiment, the hourly volumes fed to the HDS process pilot plant vary

between approximately 7 litres per hour to above 13 litres per hour. The average volume fed per hour throughout the whole experiment is however close to the aimed 10 L/h at 9.7 L/h.

6.11.1.2 The pH's throughout the Pilot Plant

The variation of pH with time in the feed and throughout the HDS pilot plant streams was measured daily and the results can be seen in Figure 6.16.

Throughout the majority of the trial, the feed pH was hovering between pH 7 and 7.5, with the Stage I Reactor and the discharge pH being generally between pH 8 and 9. Towards to the end of the trial the operating pH was raised slightly, to ensure all the metals were being removed from solution. As seen in Figure 6.16, pH increase at Reactor I led to a pH increase at Reactor II, Flocculant Tank and the discharge pH.

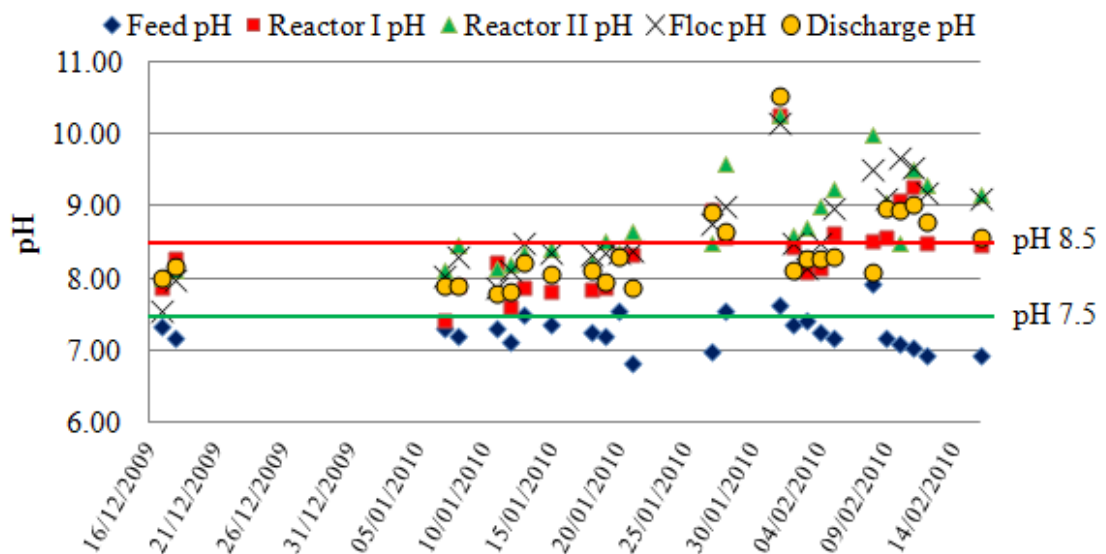


Figure 6.16 The pH variation with time in feed and throughout the HDS pilot plant streams

6.11.1.3 Water Quality

During the trial, regular samples were taken throughout the plant (influent feed, all reactors and effluent stream) in order to carry out analysis for soluble metal concentration as explained in Section 6.10.1.1 previously.

Table 6.2 Soluble concentrations in the HDS Pilot Plant feed and discharge water

Constituent	In mg/L			Out mg/L		
	Min	Max	Ave	Min	Max	Ave
Zn	24.5	76.8	42.7	0.0	5.2	1.4
Cu	0.5	3.4	1.3	0.0	0.4	0.0
Ni	4.3	8.0	6.0	0.0	3.4	1.0
Fe	0.0	0.2	0.0	0.0	0.0	0.0
Mn	12.8	26.2	16.1	0.0	11.3	6.1
Mg	17.5	36.8	22.3	5.2	27.9	20.3
Ca	200.7	470.9	339.2	87.4	391.7	290.6

Table 6.2 presents a summary of the soluble metal concentrations before (In) and after (Out) being treated by the HDS pilot plant. Results show that HDS provides efficient treatment resulting in discharge water with very low concentrations of soluble metal.

When looking at the efficiency of the HDS pilot plant in removing zinc (Figure 6.17) in more detail, it becomes evident that the efficiency in removing zinc is excellent. On average the plant is performing at a zinc removal efficiency of > 99.95%.

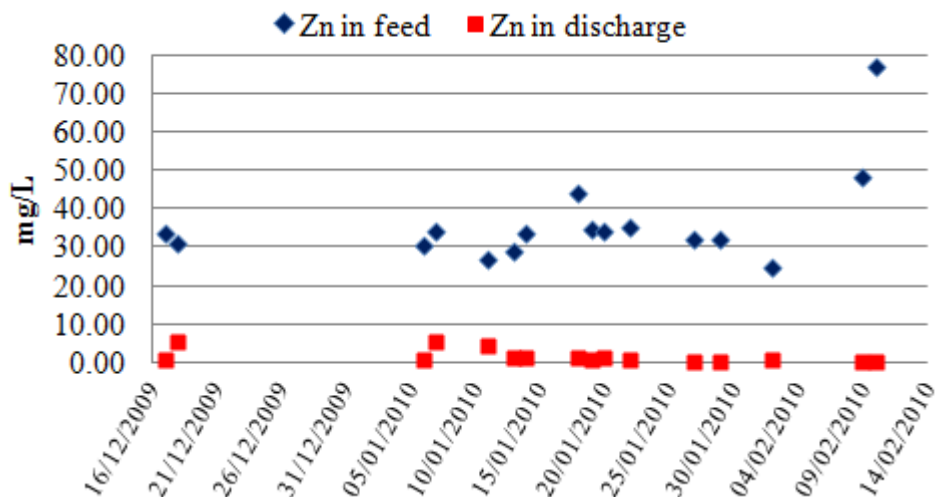


Figure 6.17 Soluble Zn concentrations with time in the HDS pilot plant feed and discharge water

Looking at the Mn and Zn removals in more detail it is interesting to note that the soluble Mn levels (Figure 6.18) in the discharge remained close to about 8 mg/L up to around 20/01/2010 when the operating pH of the Stage II Reactor was raised close to 9. The effect of increasing amounts of recirculating sludge seemed to be minimal. Once

the pH was raised the Mn concentration in the discharge decreased accordingly. For Zn, however, there appears to be a stabilisation of the soluble concentration in the pilot plant effluent well before the pH was increased.

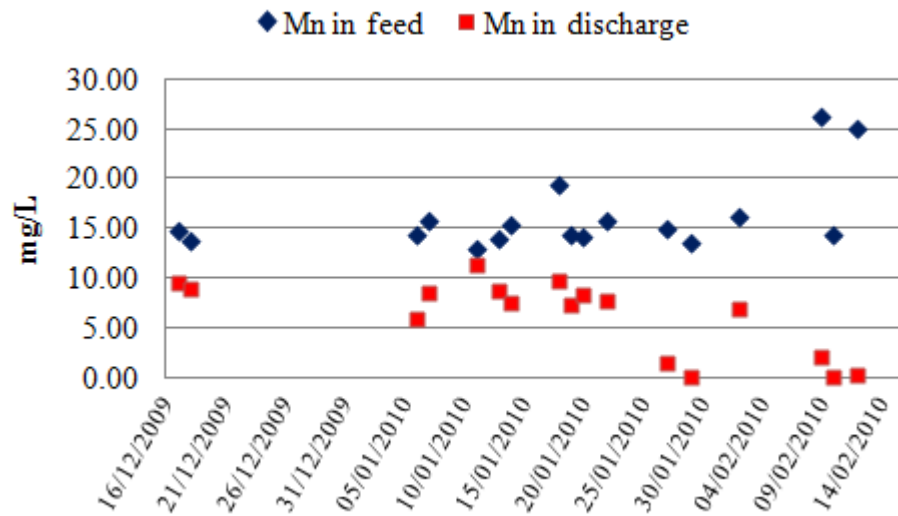


Figure 6.18 Soluble Mn concentrations with time in the HDS Pilot plant feed and discharge water

The performance of removing soluble Zn (Figure 6.17) during the trial was also getting better towards the end and lower discharge concentrations of soluble Zn were found at the end of the trial, even though the concentration of the Zn on the feed water was raised from 50 mg/L to 100 mg/L.

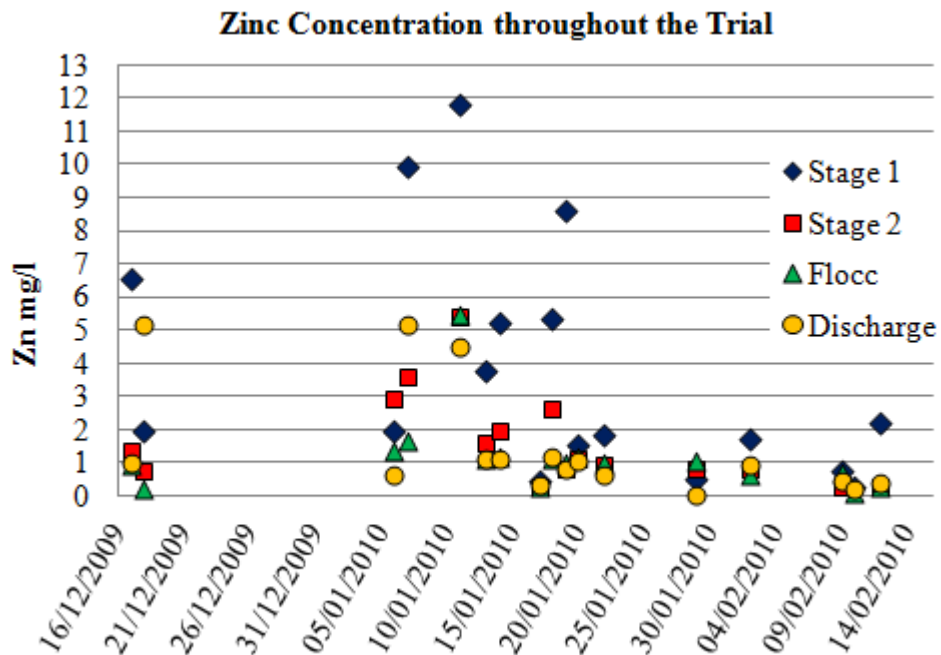


Figure 6.19 Soluble Zn concentrations with time at various locations within the HDS pilot plant, its feed and its discharge water

When looking at the soluble zinc concentrations in Reactor I and II, flocculant tank and the effluent discharge (Figure 6.19), it is clear that especially the zinc concentrations within the reactors are getting much lower when the sludge matures and its quality improves. Over all the aging of the sludge improves the zinc removal efficiency as can be seen in the Figure.

6.11.1.4 Reagent Consumption

As can be seen in Figure 6.20, the flocculant dosage rate during the trial was between 2 and just under 6 mg of flocculant per litre of feed water treated. The best settling characteristics were found with a flocculant rate of around 2.5-3 mg of flocculant per litre of feed water treated. From 20/01/2010 onwards, the flocculant dosage per litre of influent feed water was increased in order to help to increase sludge density.

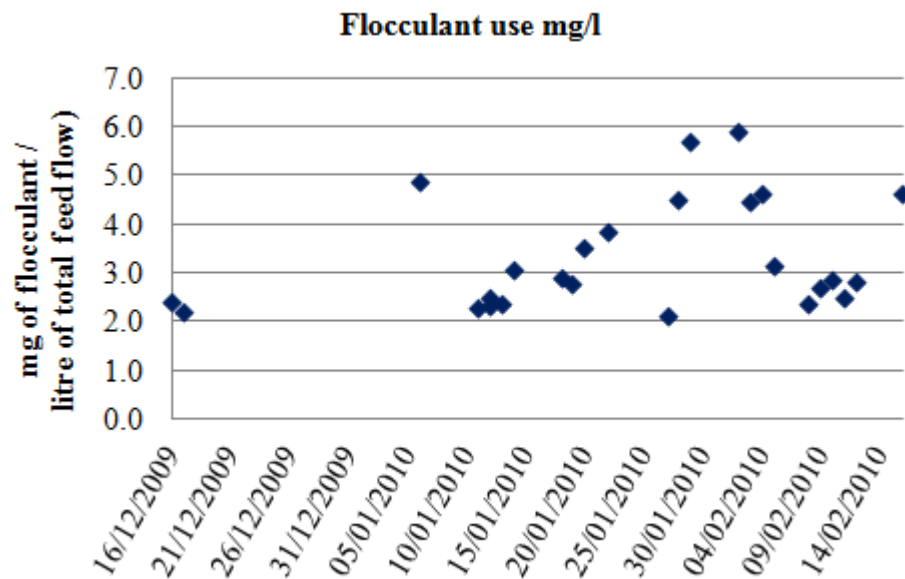


Figure 6.20 Flocculant dosage rate in mg of flocculant per litre of feed flow during the HDS pilot plant trial

When looking at the alkali consumption during the trial (Figure 6.21), it is clear that the consumption stays very similar throughout the experiment until the very end of the trial, when the metal concentrations of the influent feed were raised. The average alkali consumption during the trial is 0.2 g/L of treated water.

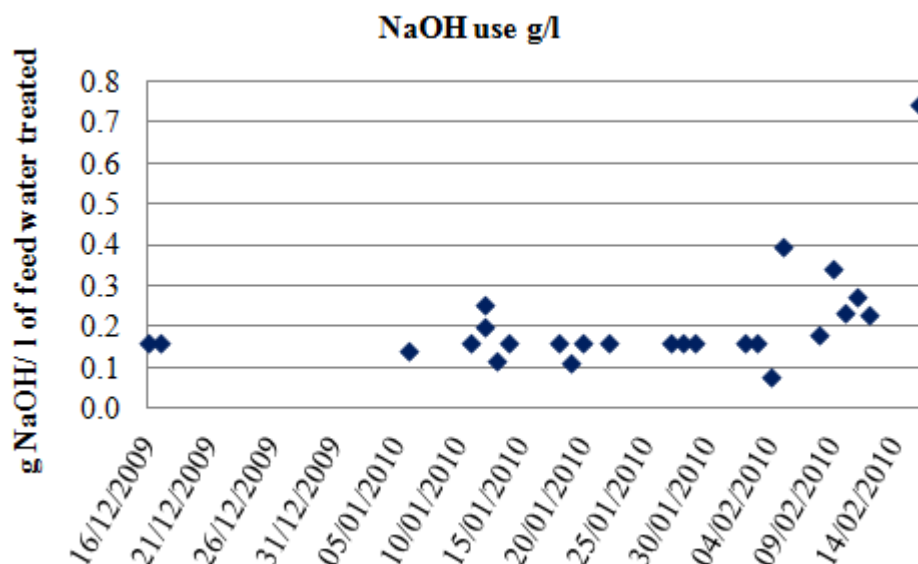


Figure 6.21 Alkali dosage rate during the HDS pilot plant trial

6.11.1.5 Sludge Density

In order to find what kind of sludge densities the staged HDS process was able to achieve whilst treating non-acid low metal concentration wastewater, regular solid concentration checks were carried out on the recirculation sludge. The checks were carried out using the total suspended solids methodology as explained in Section 6.10.1.2 of this Chapter.

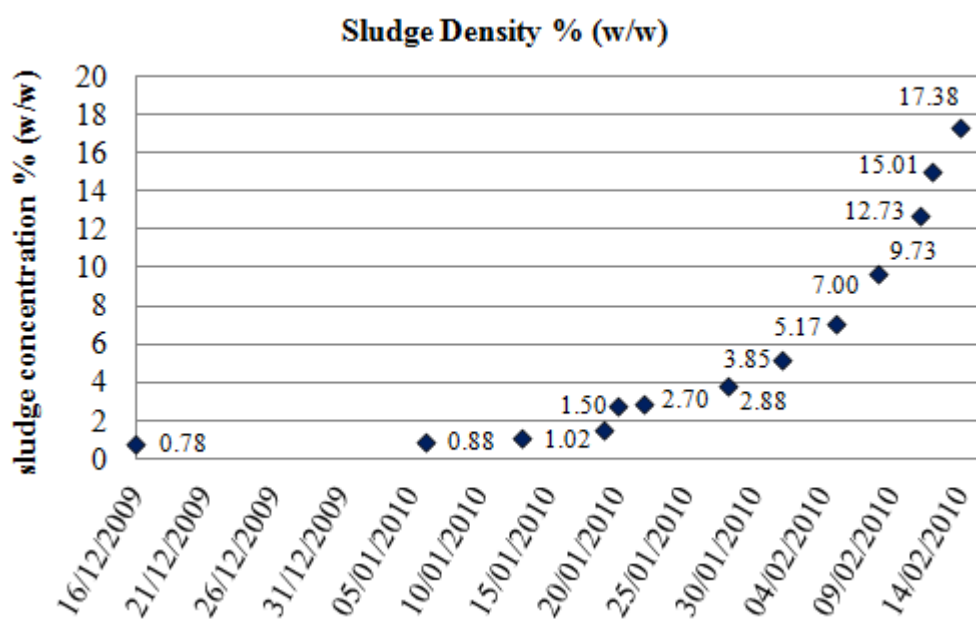


Figure 6.22 Recirculation sludge solids concentrations during the pilot plant trial

As seen in Figure 6.22, the sludge densities were very low at the beginning but during the last weeks of the experiment they started to rise rapidly. Concentrations of above 5% (w/w) were only achieved during the last two weeks of the experiment and yet the sludge densities reached those of above 17% (w/w) at the end of the experiment.

6.11.1.6 Sludge Recirculation Ratio

Regular tests were carried out in order to carefully manage the ratio of sludge recirculation in relation to the metal hydroxide mass. As explained in Section 6.4.1, the solid recirculation ratio is often measured as:

$$\frac{(\text{mass of solids recycled per unit time})}{(\text{mass of solids formed per unit time})}$$

I.e. on a weight by weight basis

Due to the low metal concentrations present at feed water, no sludge was removed from the pilot plant, although as a consequence of a blockage at the end of the trial, some sludge was lost and the sludge concentrations fell as can be seen in Figure 6.23.

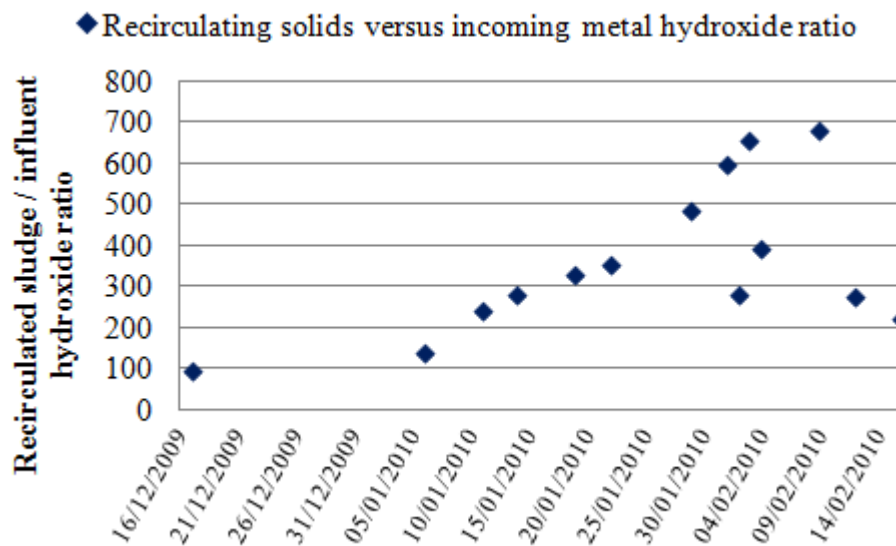


Figure 6.23 Recirculating solids and incoming metal hydroxide ratio during the HDS pilot plant trial

As seen in the Figure, the metal hydroxide mass recirculation ratio varied between 95.1:1 and 680.4:1 during the whole trial. As seen in Figure 6.22, the solids densities

were low at the beginning of the trial and they were not growing fast enough. The sludge recirculation ratio was raised significantly on 25/01/2010 in order to create denser sludge. After successfully increasing the sludge densities, the sludge recirculation ratio was lowered again at the end of the trial. It appears that higher recirculation ratio might be required when using a low metal concentration feed.

6.11.1.7 Sludge Settlement Characteristics

In order to find out how the sludge quality in terms of settling characteristics and final solid concentration changed during the HDS process experiment, settlement tests ('mudline tests') were undertaken regularly using flocculated slurry from the flocculant tank of the pilot plant. The purpose of the tests was to estimate the initial settling velocity and the final settled solids concentration.

6.11.1.7.1 Initial Settling Velocity

Daily settling tests were carried out in order to determine the settling velocity of the sludge during the HDS process experiment. The initial settling velocity tests were carried out by measuring the height of the interface between the solids and the clear supernatant water in a 250 ml measuring cylinder after 10 seconds of settling. The purpose was to determine at the initial settling velocity, which indicates the speed of the free fall of the sludge.

The initial settling velocity was calculated by dividing the distance the sludge interface had dropped by 10 seconds and the results were then plotted in m/h.

I.e.

$$\text{Initial settling velocity} = \frac{\text{distance (m) interface dropped in 10 sec}}{0.02777 \text{ (hr)}}$$

From the settling rate data collected, the initial velocities (corresponding to the linear portion of the settling curves) were plotted against the respective solids concentrations to monitor how the speed of sedimentation changes with the age of the sludge.

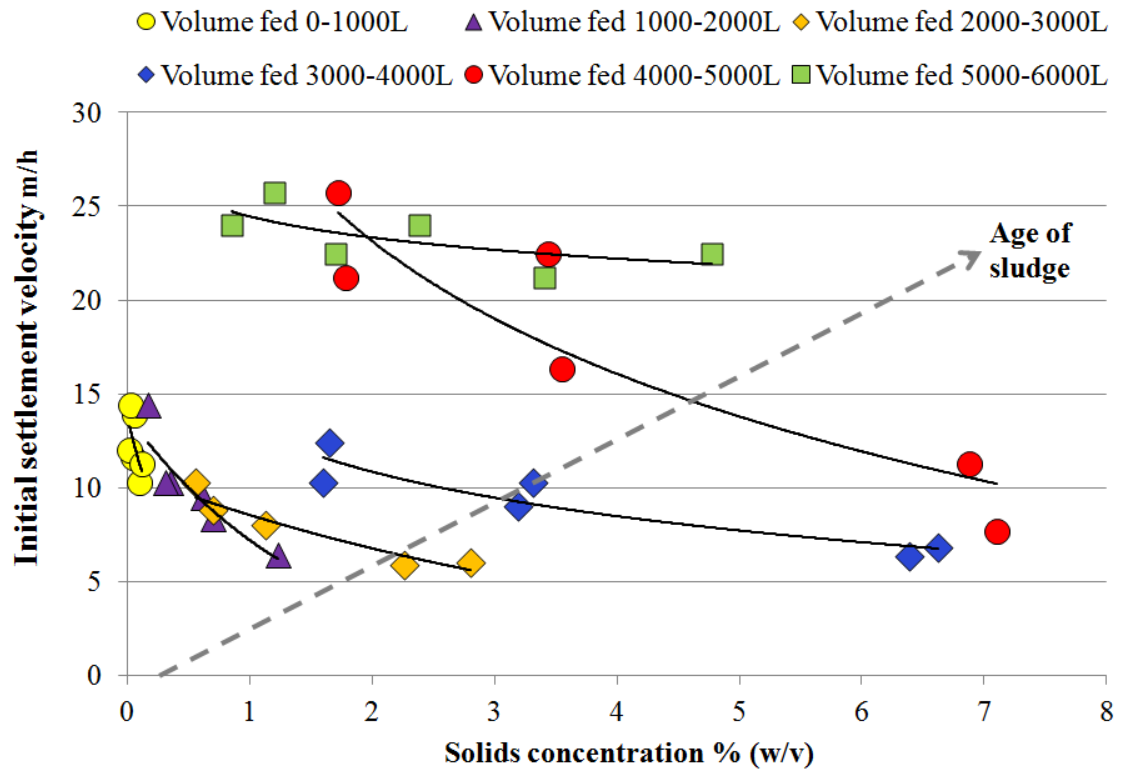


Figure 6.24 Initial Settling Rates as Functions of Volume Fed to the HDS Pilot Plant during Two Months of Operation

There was a very dramatic improvement in the settling rates as the trial progressed as can be seen in Figure 6.24, which displays the settling rates as a function of the corresponding solid concentrations for discrete ages of the sludges as reflected by the volumes treated. The ability of a floc to settle depends on its size and density. As the HDS process develops the floc density increased and an enhanced settling characteristic is obtained. The data clearly show the development of floc density (HDS formation) as more and more precipitation occurs. In total, a volume of about 6000 litres was treated over the two months of the trial, culminating in exceptionally high settling rates in excess of 22 m/h at a relatively high solids concentration of 5% (w/v). For very young sludges it was not possible to achieve high settling velocities even at solids concentrations as low as 0.1% (w/v).

6.11.1.7.2 Final Settled Solids Concentration

In order to find what the final concentrations of the settled solids would be, 250 ml sludge samples were taken from the clarifier underflow. These samples were left in a measuring cylinder for a period of 2 hours, after which the volume of the cylinder occupied by solids was used to calculate the settled solids concentration.

$$\text{Settled solids concentration} = \frac{\text{initial concentration (mg/L)} * \text{settled solids volume (mL)}}{250 \text{ mL}}$$

The initial solids concentration of the sludge was measured by filtering samples and measuring their weight against the sample volume % (w/v) after drying in oven at 105 °C for 2 hours as outlined in Section 6.10.1.2 of this chapter.

As can be seen in Figure 6.25, the final settled solids concentrations vary dramatically throughout the trial. During the first weeks of the trial, it was very difficult to get the sludge solids concentrations to increase substantially and around 330 hours of trial, equalling to approximately 2 weeks of continuous operation was necessary to get sludge with solids concentrations above 10% (w/v). Sludge concentration rose very quickly following this and after around 450 hours of operation or under 3 weeks, the sludge solids concentration was greater than 20% (w/v). Unfortunately, following the densification of the sludge, the pipe between Reactor I and II got blocked overnight on the 11th of February 2010 and most of the sludge was lost. Therefore, despite most of the sludge being mature HDS, the overall sludge concentrations dropped for 5 consecutive days, indicating that new young sludge was arising as a consequence of conventional precipitation taking place. The trial was ceased thereafter. The results of the reduced sludge concentrations can also be seen in the last solid concentrations of the sludges used for measuring the initial settling rates in Figure 6.24.

Towards the end of the trial it was demonstrated by following the whole settling curve for 24 hours that settled solids concentration in excess of 70% (w/v) were potentially achievable compared to the literature values of less than 5% (w/v) for conventional precipitation sludge, see Section 6.5

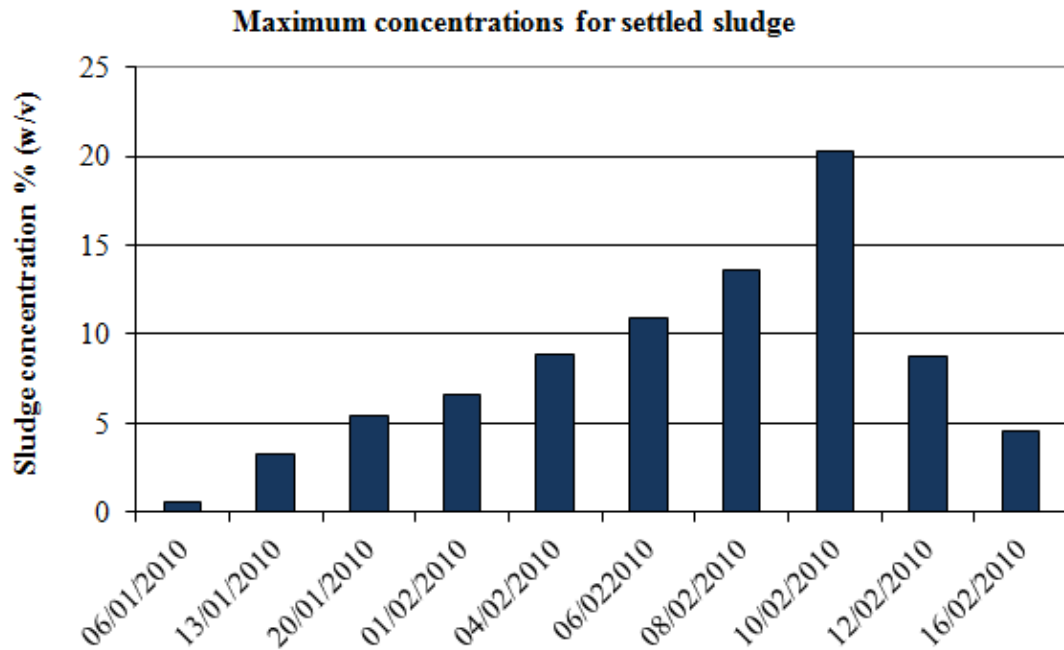


Figure 6.25 Final settled solids concentration following the whole 24 hour settling curve

6.11.2 Sludge Filtration Characteristics

As explained in detail in Section 6.12, filtration experiments were undertaken on sludges generated during the pilot plant trial and on conventional precipitation sludge.

The HDS sludge samples were taken every two weeks during the trial, with the first sample (HDS 1) taken 2 weeks after starting the experiment. The solid concentrations of the different sludges used for the experiment are listed in Table 6.3.

Table 6.3 Concentrations of sludges used for filtration experiments

Type of Sludge	Solids Conc. % (w/v)
HDS 1	3.41
HDS 2	4.50
HDS 3	4.72
HDS 4	2.94
single pass	0.79

As can be seen in Figure 6.26, where ratios of time and filtrate volumes are plotted against filtrate volumes for each sludge tested, the differences in filtration results especially between conventional single pass sludge and HDS sludges are very clear. The Figure shows that the single pass sludge has the highest slope of all the sludges, indicating that the HDS process increases sludge filterability.

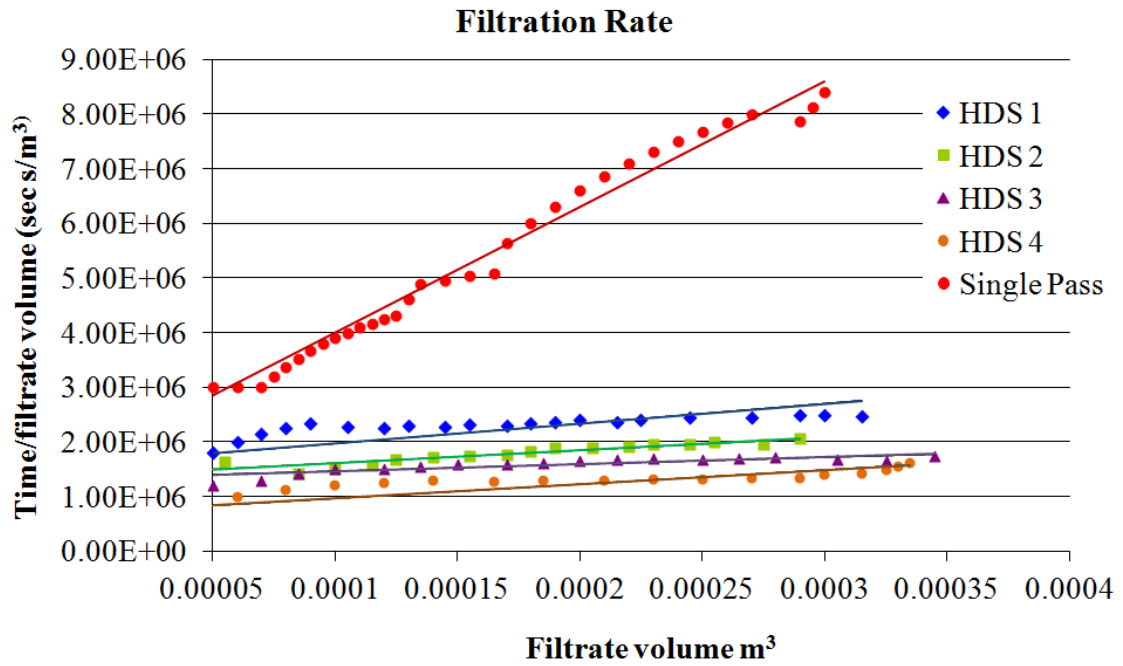


Figure 6.26 Filtration rate for incompressible cake in time/filtrate volume versus volume plot

As can be seen in Figure 6.26, there is a difference between the filtration rates of HDS sludges. The first sludge sample, HDS 1, has the highest slope, indicating slower filterability as expected. The HDS 2 and 3 sludge samples showed improved filtration rates, with the rates at the end part of the filtration volume clearly lower than those with the HDS 1 sludge sample. The final HDS 4 sample shows that the filtration rate at the beginning of the filtration is largely improved in relation to the HDS 2 and 3 and shows overall better filtration performance than the other HDS sludges. Overall, the final HDS 4 sludge is filtering around 10 times faster than the first HDS 1 sludge.

The specific cake resistance (Figure 6.27) gives an even better idea of how much better the HDS sludge quality is in relation to the single pass conventional precipitation sludges. The specific cake resistance of mixed metal single pass sludge, generated by using the same solution as the HDS pilot plant influent feed, has a specific cake

resistance of nearly 35 000 Gm/kg, whereas after some weeks of operation, the pilot plant HDS sludges have a cake resistance of a mere 169 Gm/kg, over 200 times less than the conventional precipitation sludge.

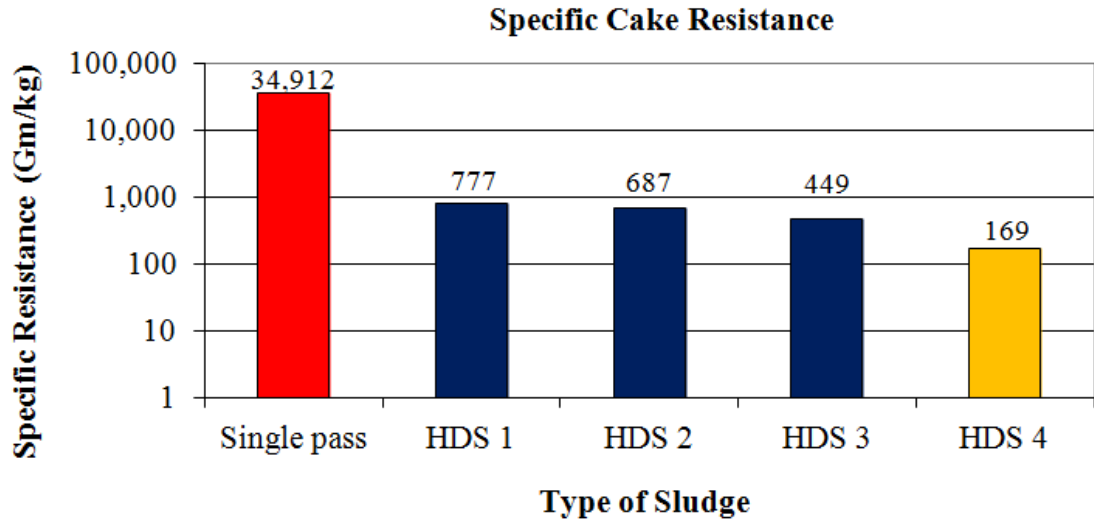


Figure 6.27 Specific cake resistance for different sludges

The reason for the specific cake resistance for the HDS sludges getting lower is that when the sludge matures due to the fact that the slope of the filtration time/volume versus volume plot is getting smaller (Figure 6.26) as is the pressure drop across the sludge cake. Furthermore, the viscosity of the filtrate and the dry cake mass per unit volume of filtrate is getting higher (Equation 6.2).

6.12 Observations

Several observations were made during the trial. These include:

- The pH control of the HDS process pilot plant is imperative. This supports the finding of Aubé, et al. (1997).
- HDS can be formed using sodium hydroxide as an alkali and influent feed with low iron concentrations, supporting the finding of Bullen (2006).
- HDS can be formed using low total metal concentration and non-acidic water, despite of previous beliefs.

- There is an indication that higher sludge recirculation ratios might be required when using influent feed with low metal concentrations. More research into the topic would be required to confirm this.
- It appears that when high concentrations of non-metal ions are present, including chloride, calcium and magnesium, higher recirculation ratios are required. This supports the findings of Bullen (2006).

6.13 Conclusion

The use of HDS started in the steel industry (pickle liquor) and has since been recognised as the preferred active treatment method for mine water, especially AMD, but it has never before been tested with low metal concentration nor non-acidic effluent.

In the HDS process, the arisen sludge is recycled from the clarifier and is mixed with alkali prior to adding the incoming effluent or effluent prior to adding the alkali. During HDS process, the recycling of the previously precipitated sludge results in solids crystallisation, creating denser and heavier sludge particles.

The HDS process provides many benefits, including improved treatment efficiency and sludge quality, and up to 50% cost savings on sludge handling and disposal

The results of the continuous staged or Type II HDS process pilot trials mimicking steelworks final effluent at the Tata site in Port Talbot prove that matured high density sludge > 17% (w/v) settling at a rate of 22 m/h can be created by using:

- Low iron influent concentrations
- Sodium hydroxide (NaOH) as a reagent

These findings support the findings of Bullen (2006) and contradict the findings of many other HDS process experts.

Furthermore, the results show that despite previous beliefs, High Density Sludge forms using the following parameters:

- Low overall total influent metal concentration and
- Non-acidic influent water.

HDS forms very readily with this particular steelworks feed, giving precipitates with excellent settling characteristics.

Furthermore, it was found that HDS sludge created by using influent feed that mimics steelworks effluent is up 200 times easier to filter than single pass sludge.

7 CONCLUSIONS

The main conclusions from the research work reported in this thesis are as follows:

- The Water Framework Directive (WFD) 2000/60/EC is set to overhaul the management of the water environment within the EU and will have a significant effect on water management within steelworks.
- A large amount of around 145,000,000 m³ (2007) of water is being used in the Port Talbot Steelworks over a year and around 12,500,000 m³ is discharged annually to the Bristol Channel via the Long Sea Outfall. Out of the total effluent, around 3,500,000 m³ per annum is treated by the Nautilus final effluent treatment plant.
- The Nautilus chemical precipitation treatment system performs generally well, removing around 80% suspended solids present in the influent feed, although on occasions breaches in the consent limits, particularly for Zn, do occur.
- As a part of the World Steel Association Water Management Working Group project, 29 steel plants, including 17 integrated and 12 non-integrated, completed the survey, representing around 8% or 110.9 million tonnes of the World's annual steel output.
- On a worldwide basis the Working Group has found that most of the water consumed during steel making is used for supporting functions, including cooling for power generation. Water consumption at different steel plants varies from 1 to near 150 m³ per tonne of steel and most of the steelworks rate their water management activities high, despite their water related performance (m³/ts) figures.
- Iron enhances zinc precipitation strongly via co-precipitation. A similar effect, although to a lesser extent, was achieved in zinc co-precipitation with nickel and lead.

- The results of the continuous staged (or Type II) HDS process pilot trials mimicking steelworks final effluent at the Tata site in Port Talbot proved that matured high density sludge containing more than 17% (w/w) solids concentration settling at a rate of 22 m/h can be created.

Furthermore, the results show that despite previous beliefs, High Density Sludge forms using:

- Low overall total influent metal concentration containing low levels of Fe,
 - Non-acidic influent water and
 - Sodium hydroxide (NaOH) as the alkaline reagent.
-
- HDS sludge created by using an influent feed that mimics steelworks final effluent is up to 200 times easier to filter than single pass (i.e. freshly precipitated without sludge recirculation) sludge.

8 RECOMMENDATIONS

Based on the results of this research project, several recommendations for water in steelworks particularly in Port Talbot can be derived, including:

Nautilus final effluent treatment system

- For zinc using NaOH in a conventional precipitation system, a pH of around 10 should be applied as proven by the laboratory tests, despite the optimum pH for Zn removal theoretically being closer to 9.
- Effluent treatment systems targeting zinc removal should be operated continuously and zinc precipitates are likely to dissolve back to solution if they are left standing over night and changes to the physical characteristics of zinc precipitates have been reported to occur on standing at pH between 10.5-11.
- Currently flocculant is used randomly, but use should be calculated using stoichiometry and the dosing should also be confirmed by laboratory tests during the runs as stoichiometric values are theoretical and can often be too high. By using too little or too much flocculant, settling suffers.

Transformation of Nautilus final effluent treatment system into a HDS Process

In order to transform Nautilus final effluent treatment into a HDS Process, several changes need to take place. A simplified process diagram of one possible new solution can be seen in Figure 8.1 below.

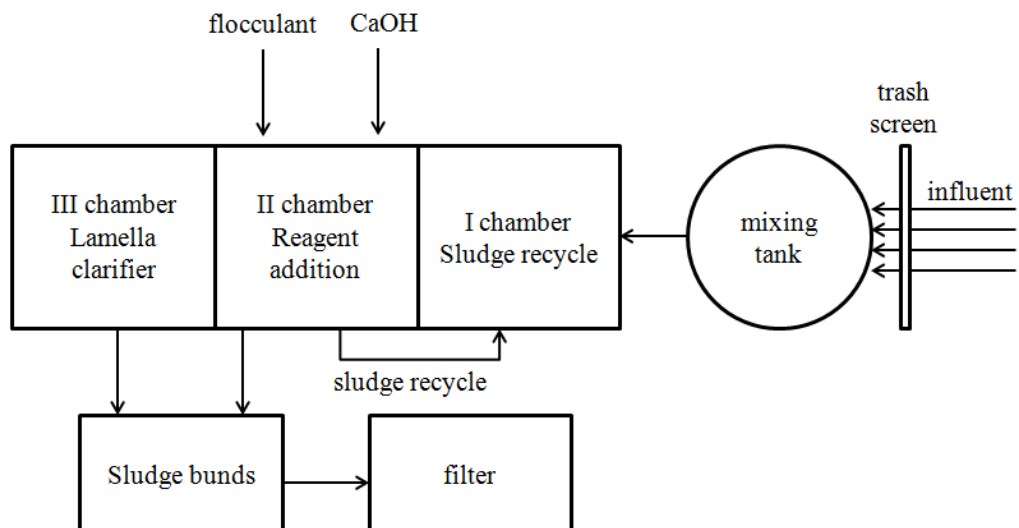


Figure 8.1 Suitable design for Nautilus HDS Process

In the new design, the influent streams arriving to the Nautilus HDS Process treatment systems would be pumped through a trash screen into a mixing tank. The purpose of the mixing tank is to provide unified effluent streams to the new Nautilus effluent treatment plant. The mixing tank should have a two-hour influent flow capacity.

From the mixing tank the homogenous effluent is pumped to the first chamber, where it is mixed together with the recirculated sludge that acts as a seed and a platform for the precipitation to take place. Additionally, air could be added to this chamber to allow iron oxidation to valence III, which would enhance co-precipitation behaviour.

From the first chamber, the effluent overflows to the second chamber, where reagents are added. The alkali used could be changed into calcium hydroxide, which is cheaper than sodium hydroxide. Flocculant is also added in this chamber. Reagent should be applied based on stoichiometry and laboratory tests. Changing into a HDS Process will lower reagent and flocculant consumption. Part of the sludge generated during this step will be recirculated to the first chamber, the rest is pumped from underneath the chamber to the sludge bunds. From the sludge bunds the sludge is pumped to a suitable filter for further dewatering.

From the second chamber, the effluent overflows to the third chamber, where oil and smaller particles are separated by lamella clarifier. The generated sludge is pumped to the sludge bunds and further to the filter.

The above described Nautilus HDS Process would require several changes to the current systems. These include among others:

- Investing into new equipment, including feed mixing tank, trash screen and suitable filter.
- Raising the walls of the treatment system, so that it would be possible to divide the treatment system into 3 separate chambers and enable water overflow from one section to another.
- Arranging sludge removal from underneath the second chamber and changing the currently used sludge pumps to properly efficient sludge pumps.

- Have a more controlled management of the Nautilus effluent treatment plant and transforming it to a HDS Process means running the plant more carefully due to ensure right parameters, including the correct sludge recycle ratio.

Overall Port Talbot Steelworks water systems

Sufficient metering should be installed to the water and effluent systems in order to manage the water and effluent flows.

Facility-specific water systems

It is most efficient and cost-effective to treat the effluent at source, therefore it would be beneficial to improve some of the facility-specific treatment systems, including:

- New water treatment system for the Hotmill in order to create a fully closed-loop recirculating water system and to remove steel scale present in the effluent. A suitable treatment system could include, for example, efficient clarifiers/thickeners, followed by sand filters and a suitable filter for solid/liquid separation.
- Taking the Coke-Ovens DETOX biological effluent treatment system back into use.
- New water treatment system for the Blast Furnaces gas washing effluent treatment. This effluent contains most of the zinc present in the steelworks effluent flows and a suitable treatment system tackling volatile metals within the effluent could include a process with an efficient aeration tank, followed by a suitable clarifier/thickener.

worldsteel Water Management Working Group

- Investigate how the findings of the worldsteel Water Management Working Group could be put in to use at the Port Talbot Steelworks. Specifically, the best practice descriptions that can be found within the The worldsteel (2011) 'Water Mangement in the Steel Industry' could be used as a part of the development of the water systems within Port Talbot Steelworks.
- worldsteel is organising a second stage of the Water Management Working Group and it would be beneficial if someone from the Port Talbot Steelworks that is familiar with the water systems would take part on the Working Group's activities.

9 FUTURE WORK

Following the investigations described in this thesis, a number of projects concentrating on the HDS Process could be taken on. Ideal topics for further research include:

- Further investigations on how HDS formed from steelworks feed mimicking influent affects filterability and what kind of filter would be most suitable for use for this type of HDS.
- Further investigations into the formation of HDS using:
 - Influent with low metal and especially low iron concentrations,
 - Influent with Zn as the main metal in solution,
 - Non-acid influent and
 - Other than calcium-based alkali.

Investigations into the formation of HDS using the above parameters should concentrate in finding suitable pH range for a minimal zeta potential in order to ensure minimum electrokinetic potential within the flocs and therefore minimal stability of the colloidal system, aiding flocculation. In order to get a better understanding on the HDS formation and sludge particle structure, crystal or otherwise, investigation should include characterisation by scanning electron microscope (SEM).

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11 APPENDICES

11.1 Appendix I Publications