

Iodide Retention by Modified Kaolinite in the Context of Safe Disposal of High Level Nuclear Waste

S. Sivachidambaram¹ and Sudhakar M. Rao²

Abstract: Bentonite clay is identified as potential buffer in deep geological repositories (DGR) that store high level radioactive wastes (HLW) as the expansive clay satisfies the expected mechanical and physicochemical functions of the buffer material. In the deep geological disposal of HLW, iodine-129 is one of the significant nuclides, attributable to its long half-life (half life = 1.7×10^7 years). However, the negative charge on the basal surface of bentonite particles precludes retention of iodide anions. To render the bentonite effective in retaining hazardous iodide species in DGR, improvement of the anion retention capacity of bentonite becomes imperative. The iodide retention capacity of bentonite is improved by admixing 10 and 20% Ag-kaolinite (Ag-K) with bentonite (B) on a dry mass basis. The present study produced Ag-kaolinite by heating silver nitrate-kaolinite mixes at 400°C. Marginal release of iodide retained by Ag-kaolinite occurred under extreme acidic (pH = 2.5) and alkaline (pH = 12.5) conditions. The swell pressure and iodide retention results of the B-Ag-K specimens bring out that mixing Ag-K with bentonite does not chemically modify the expansive clay; the mixing is physical in nature and Ag-K presence only contributes to iodide retention of the admixture. DOI: 10.1061/(ASCE)HZ.2153-5515.0000121. © 2012 American Society of Civil Engineers.

CE Database subject headings: Bentonite; Radioactive wastes; Waste management.

Author keywords: Bentonite; Iodide; Radionuclides; Repository; Retention.

Introduction

In the deep geological disposal of radionuclides, iodine-129 is one of the significant nuclides, attributable to its long half-life (half life = 1.7×10^7 years) and tendency to easily migrate out of the geological repository into the biosphere caused by its high solubility and poor sorption onto most geologic media (Sazarashi et al. 1994; Balsley et al. 1998). Therefore, studies have focused on developing methods for immobilization of iodide ions with a view to apply these results toward iodide retardation in the geological repository environment. Balsley et al. (1998) examined the iodide sorption capacity of copper sulfides, imogolite-rich soils, hydrotalcites, copper-oxides, lignite coal, and calcium monosulfate aluminate toward iodide ions and observed that the iodide ions have preference to specific minerals depending on the solution pH. Sazarashi et al. (1994) observed that iodide ions are not appreciably adsorbed on minerals, such as allophane, attapulgite, and montmorillonite. Toyohara et al. (2000) examined the iodide sorption capacity of mixed alumina cement-calcium compounds. Their experimental results suggested that iodide sorption by calcium aluminate occurs by replacement of hydroxyl ions by iodide ions. Balsley et al. (1998) also noted that specific cement phase-calcium monosulfate aluminate hydrate possess a high sorption capacity for iodide ions.

¹Research Student Centre for Sustainable Technologies, Indian Institute of Science, Bangalore 560012, India. E-mail: sivani@astra.iisc.ernet.in

²Professor, Dept. of Civil Engineering and Chairman, Centre for Sustainable Technologies, Indian Institute of Science, Bangalore 560012, India (corresponding author). E-mail: msrao@civil.iisc.ernet.in

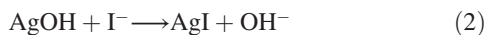
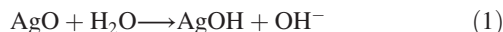
Note. This manuscript was submitted on October 15, 2010; approved on June 29, 2011; published online on July 1, 2011. Discussion period open until December 1, 2012; separate discussions must be submitted for individual papers. This paper is part of the *Journal of Hazardous, Toxic, and Radioactive Waste*, Vol. 16, No. 3, July 1, 2012. ©ASCE, ISSN 2153-5493/2012/3-192-200/\$25.00.

The canisters containing the HLW on placement in DGR need protection against tectonic activities and chemical attack by dissolved elements and from microbes (Pusch 2008). Densely compacted bentonite is identified suitable for this purpose because of its large swell potential, low permeability, sufficient bearing capacity, and high cation adsorption capacity (Pusch 2008). By virtue of negatively charged basal surface, bentonite clay has negligible affinity for retention of anions (van Olphen 1963). Attempts have been made to improve the iodide retention capacity of bentonite by treating the clay with cationic polymers (Dultz and Bors 2000; Riebe et al. 2005; Kaufhold et al. 2007). In a recent study, Inyang et al. (2007) examined the effect of aqueous polymers on the swelling of sodium montmorillonite. Their results illustrated that the cationic polymer polyacrylamide reduces the volumetric swelling ratio of sodium montmorillonite by 40% relative to distilled water. Polycations are almost irreversibly adsorbed by Coulombic interaction on the clay surface (Breen 1999), which is apparently responsible for the reduction in swell potential of sodium montmorillonite clays on treatment with cationic polymers. To circumvent this problem, Kaufhold et al. (2007) resorted to adding 5% of hexadecylpyridinium treated bentonite to 95% MX-80 bentonite; this small addition was observed not to affect the swelling pressure of compacted MX-80 clay. As large swell potential is a key property of bentonite buffer to maintain tight contact between the canisters and the surrounding rock and treatment with polycations may possibly reduce the swelling capacity, an alternate method for improving the iodide sorption capacity of bentonite is examined.

Scope of the Study

Sazarashi et al. (1994) observed that minerals, such as mercury sulfide (HgS, Cinnabar) containing metal ions capable of forming insoluble iodides (mercury iodide) have higher adsorption capacities for iodide ions than minerals that retain anion

through ion-exchange reactions. In addition to mercury, silver compounds such as silver oxide form insoluble halides through reactions of the type (Cotton et al. 1995)



Daniels and Rao (1983) examined the sorption of silver ions by kaolinite at room temperature (25°C) and elevated temperatures (255–290°C). The workers noted that 35 meq/100 g, 63 meq/100 g, 83 meq/100 g, and 106 meq/100 g, of silver ions are sorbed by kaolinite at temperatures of 25°C, 255°C, 275°C, and 290°C, respectively. Guided by the increased amounts of silver retention at elevated temperatures, the present study produced Ag-kaolinite by heating silver nitrate-kaolinite mixes at 400°C. Bentonite-Ag-kaolinite mixes containing 0, 10%, and 20% Ag-kaolinite on a dry weight basis are prepared and examined for iodide sorption from aqueous sodium iodide solutions. Iodide measurements were performed using ion chromatograph method. This study presumes that the results obtained for nonradioactive iodide-127 species employed would be applicable to the radioactive iodide-129 species encountered in deep geological repositories for HLW. The Ag-kaolinite content in the bentonite mix is restricted on the basis of the I-127 concentrations encountered under field conditions and the effect of Ag-kaolinite dilution on the swell pressure of the compacted mixes.

Materials and Methods

Commercially obtained kaolinite (Alminrock and Chemicals, Bangalore, India), natural bentonite from Rajasthan, India, analytical reagent grade silver nitrate (AgNO_3), and sodium iodide (NaI) salts were used in the laboratory experiments. The physical and chemical properties of kaolinite and bentonite specimens are provided in Table 1. The specific gravity of kaolinite and bentonite were determined as per Bureau of Indian Standards (BIS) (1980a) and corresponds to 2.64 and 2.69, respectively. The grain size distributions of the clay specimens were determined as per BIS (1985a). Kaolinite is mostly a silty material (silt fraction = 87%, size range 75 to 2 μ) with 12% clay-sized fraction (< 2 μ), whereas the bentonite predominates in clay-sized fraction (86%). The Atterberg limits of kaolinite and bentonite were determined as per BIS (1985b). Kaolinite has liquid limit of 31% and plasticity index of 3%, and classifies as ML as per Unified Soil Classification System (USCS). Despite its silty nature, the mineral is essentially composed of kaolinite as revealed by the XRD pattern in Fig. 1 that shows prominent peaks at 0.714, 0.314, and 0.234 nm characteristic of this 1:1 nonexpanding mineral. Comparatively, bentonite has a liquid limit of 314% and plasticity index of 279%, and classifies as CH as per USCS classification for inorganic clays of high plasticity. The compaction characteristics of the clay minerals were determined as per BIS (1980b). The standard Proctor maximum dry density (MDD) and optimum moisture content (OMC) values of bentonite, correspond to 1.37 Mg/m^3 and 29%; the corresponding values for kaolinite and Ag-kaolinite were 1.40 Mg/m^3 and 31% and 1.39 Mg/m^3 and 30%, respectively.

The external surface of kaolinite was determined by the BET N_2 adsorption method and corresponds to 8 m^2/g . The total surface area of bentonite was determined by the ethylene glycol adsorption method (Pennell 2002) and corresponds to 551 m^2/g . The exchangeable calcium, magnesium, sodium, and potassium ion contents of kaolinite and bentonite specimens were determined

Table 1. Physical and Chemical Properties of Kaolinite and Bentonite

Property	Kaolinite	Bentonite
Specific gravity	2.64	2.69
Particle size distribution (%)		
Sand	1	2
Silt	87	12
Clay	12	86
Liquid limit (%)	31	314
Plasticity index (%)	3	279
USCS classification	ML	CH
MDD (Mg/m^3)	1.40	1.37
OMC (%)	31	29
Surface area (m^2/g)	8	551
CEC (meq/100 g)	2.1	81
Ca	0.6	18
Mg	0.6	15
Na	0.8	47
K	0.1	1
Chemical composition (%)		
SiO_2	51	60
Al_2O_3	33	18
Fe_2O_3	1	10
CaO	0.15	2
MgO	0.13	2
Na_2O	0.22	2
K_2O	0.2	2
Loss on ignition (%)	13.5	4

by equilibrating the specimens with neutral 1 M ammonium acetate solution to displace the exchangeable calcium, magnesium, sodium, and potassium ions by ammonium ions (Hesse 1971). The cation exchange capacity (CEC) of the clay specimens were determined by summing the concentrations of the displaced calcium, magnesium, sodium, and potassium ion contents. The concentrations of the displaced calcium, sodium, and potassium and magnesium ions were determined using an inductively coupled plasma-optical emission spectrometer (ICP-OES). Kaolinite has a CEC of 2.1 meq/100 g and bentonite has a CEC of

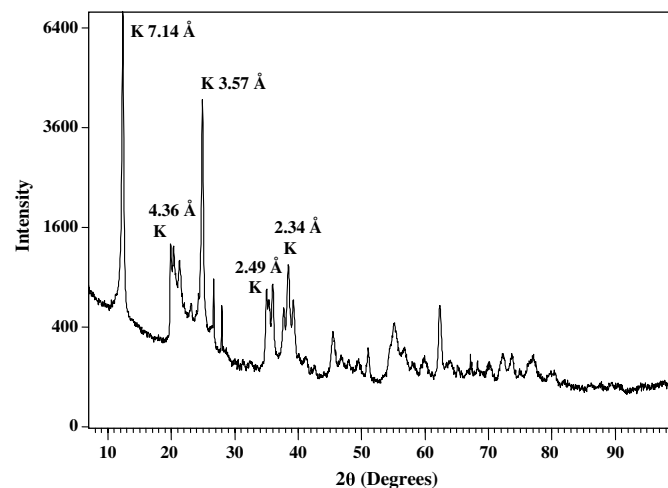
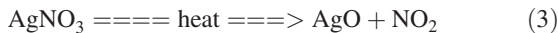


Fig. 1. XRD pattern of kaolinite

81 meq/100 g. The chemical composition of kaolinite and bentonite were determined by digesting the clays using microwave digester and determining the inorganic constituents in the acid extract by ICP-OES (Hossner 2002).

Silver Sorption and Kinetics Experiments

Silver nitrate melts at 212°C and decomposes on heating at temperature of 440°C (Perry et al. 1999) according to the reaction



The thermogram in Fig. 2 illustrates that silver nitrate decomposition commences around 400°C. Decomposition of AgNO_3 to AgO should yield 27% weight loss through the reaction (3). The thermogram in Fig. 2 illustrates that AgNO_3 experiences approximately 45% weight loss on heating at 400°C. The additional weight loss is attributed to loss of adsorbed water molecules from the silver nitrate crystals. Because thermal decomposition of silver nitrate to AgO is a prerequisite for iodide retention (reactions 1 and 2), the silver nitrate-kaolinite mixtures were heated at 400°C. A 20% silver nitrate-80% kaolinite mixture (on dry mass basis) was selected as preparation for the silver-kaolinite phase, as sorption experiments with 1%, 5%, 10%, 20%, 25%, and 30% silver nitrate-kaolinite mixes revealed that silver retention by kaolinite reaches near equilibrium at this silver nitrate concentration (Fig. 3). Further, the heating duration was restricted to 30 min as kinetic experiments conducted with 20% silver nitrate-80% kaolinite mixes illustrated the amount of silver retained by kaolinite attained equilibrium for this heating period (Fig. 4). In the sorption and kinetics experiments, the heated silver nitrate-kaolinite mixtures were washed with distilled water until the washings were free of unreacted silver ions; the washed samples were oven-dried at 105°C and stored in amber bottles until use. The total amounts of silver retained by kaolinite in the sorption and kinetics experiments were estimated by dissolution of the washed silver-kaolinite samples in a microwave digester and determination of the dissolved silver in the digester extract using an inductively coupled plasma-optical emission (ICP-OES) spectrometer. The washed and oven-dried specimens obtained by heating the 20% silver nitrate-80% kaolinite mixture at 400°C for 30 min are referred as Ag-kaolinite specimens. The Ag-kaolinite will be designated as Ag-K in further discussions, whereas bentonite is designated as B.

Characterization of Ag-Kaolinite

To estimate the amount of exchangeable silver, the Ag-K specimen was extracted with neutral ammonium acetate solution and the amount of silver in the ammonium extract was determined using the ICP-OES method. The difference between the total silver and exchangeable silver estimated the amount of nonexchangeable

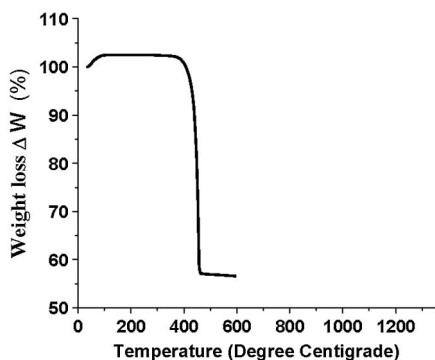


Fig. 2. Thermogram of silver nitrate

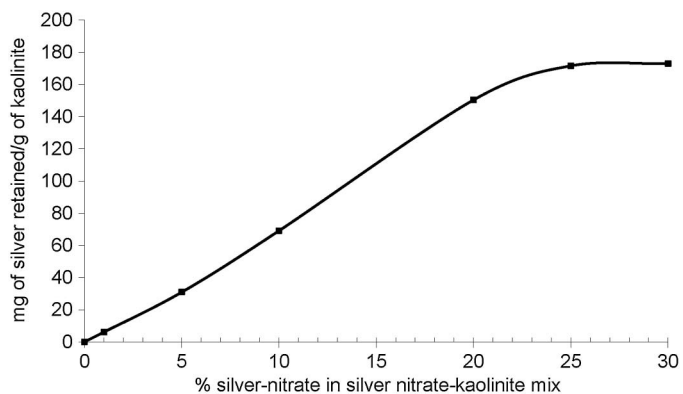


Fig. 3. Influence of initial silver nitrate concentration on silver retention by kaolinite

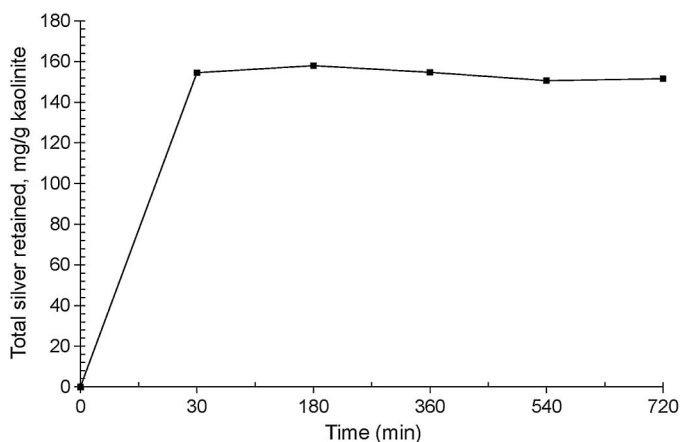


Fig. 4. Time-rate of silver retention by kaolinite

silver available in the Ag-K specimen. X-ray diffraction (XRD) analysis (2θ range, 5–15°, scan rate 1°/min) were performed with kaolinite and Ag-K specimens. Differential scanning calorimetry (DSC) analyses were performed with silver nitrate salt from ambient (25°C) to 1,500°C at a heating rate of 10°C/min.

The external surface area of Ag-K was determined by BET N_2 adsorption method and corresponds to 7 m^2/g ; its cation exchange capacity determined by ammonium acetate extraction corresponds to 1 meq/100 g.

Iodide Sorption by Ag-Kaolinite and Ag-Kaolinite + Bentonite Specimens

Iodide sorption by Ag-kaolinite (designated as Ag-K), 90% bentonite + 10% Ag-K specimen (designated as 90B-10AgK), and 80% bentonite + 20% Ag-K specimen (designated as 80B-20AgK) was determined as function of initial iodide concentration to estimate the iodide retention capacity of each mix. In these experiments, 0.5 g of the material was equilibrated with 50 ml batches of NaI solutions (iodide concentration range, 90 mg/L to 1,000 mg/L) for 30 min using a horizontal mechanical shaker. The 30 min duration was on the basis of the results of the separately conducted kinetics experiments whose results are not reported in the present study. At the end of the given equilibration period in the retention capacity experiments, the suspensions were filtered and the iodide concentrations in the filtrates were determined by ion chromatograph method. The difference between

initial and final iodide concentration was used to calculate the amount of iodide retained by the Ag-K and B-Ag-K specimens. Ag-K specimen contacted with 1,000 mg/L iodide solution for 30 min was subjected to XRD analysis to detect any AgI (silver iodide) phase formation. To examine the influence of longer contact period on iodide sorption, 0.5 g of Ag-K was also agitated with 50 ml of 1,000 mg/L iodide solution for 24 h; following agitation, the amount of iodide retained by Ag-K was calculated as described previously. The amount sorbed after 24 h of equilibration (59 meq/100 g) was near identical to that sorbed after 30 min of equilibration (58 meq/100 g).

All other factors being similar, the capacity of Ag-K to retain iodide ions would depend on the purity of the kaolinite mineral and the fines content (silt + clay fractions). As previously noted, the XRD pattern of kaolinite (Fig. 1) shows reflections pertaining to kaolinite alone. Presence of other clay minerals, for example illite/montmorillonite, would tend to reduce the silver sorption and, in turn, the iodide sorption values. Similarly, the kaolinite used in the study is characterized by 99% fines content (Table 1, silt = 87% and clay = 12%). Reduction in fines content would reduce the sorption sites for silver uptake and, in turn, the iodide sorption.

Leaching tests were performed with iodide sorbed Ag-K specimens at pH ranging from 2.5 to 12.5. Iodide sorbed Ag-K specimens were produced by agitating Ag-K with 500 mg/L iodide solution for 30 min. After agitation, the clay material was filtered and repeatedly washed with distilled water to remove free iodide. The washed specimens were agitated (using mechanical shaker) with strongly acidic (pH = 2.5) to strongly alkaline (pH = 12.5) aqueous solutions for 1 h; the suspensions were filtered and iodide concentrations in the filtrates were measured using ion chromatograph. The pH of the aqueous solutions was adjusted using 0.001 MHN O₃ and 0.001 M NaOH solutions.

Zeta Potential Measurements

Zeta potential measurements were performed on kaolinite and Ag-K specimens to investigate the changes in surface charge characteristics of kaolinite on silver sorption and of Ag-K specimen on iodide sorption at range of pH values (3–11). The zeta potential measurements were performed using electroacoustic method that automatically measured the zeta potential of the clay suspensions (2% suspension on weight basis) as a function of pH at 25°C. Potassium nitrate (0.001M) was employed as the electrolyte in the zeta potential measurements on kaolinite and Ag-K suspensions. To examine the influence of iodide sorption on the surface charge characteristics of Ag-K specimen, zeta potential measurements were performed on Ag-K suspension (1.9%) using 0.01 M sodium iodide solution as the electrolyte solution at range (3–11) of pH values. The 1.9% Ag-K suspension refers to 1.9 g of mineral suspended in 100 ml of 0.01 M sodium iodide solution.

Swell Potential and Swell Pressure Measurements

Oedometer swell potential tests were performed using compacted bentonite and 80B-20AgK specimens. The bentonite and 80B-20AgK specimens were remolded with a known volume of distilled water to yield specimens characterized by 25% moisture content (corresponding to standard Proctor optimum moisture content of the 80B-20AgK specimen); the moist specimens were statically compacted in 76-mm diameter oedometer rings (specimen thickness = 8 mm) to dry density of 1.5 Mg/m³ (corresponding to standard Proctor maximum dry density of 80B-20AgK). The standard Proctor MDD and OMC values of bentonite (1.37 Mg/m³ and 29%) differ from those of the 80B-20AgK specimen (1.5 Mg/m³ and 25%). However, bentonite

was tested at the same dry density and water content as the 80B-20AgK specimen as the swell percent and swell pressure are affected by the compaction characteristics of the clay (Rao 2006). The compacted clay specimens were inundated with distilled water at net vertical stress of 6.25 kPa in separate oedometer assemblies. The swelling strains of the compacted specimens were monitored until they became nearly constant. Periods ranging from 20 to 22 days were needed for the swelling strains of the compacted specimens to become constant. The percent swell of the compacted specimens on inundation with distilled water at time interval t was calculated as

$$\% \text{swell} = \frac{\Delta H}{H_i} \times 100\% \quad (4)$$

In Eq. (4), ΔH represents the increase in height of the wetted specimen at time t and H_i represents the initial height of the compacted specimen.

Swell pressure measurements were performed with compacted (dry density = 1.50 Mg/m³ and moisture content = 25%) bentonite, 90B-10AgK, 80B-20AgK, 70B-30AgK, and 50B-50AgK specimens using the constant volume method. The compacted specimens contained in conventional oedometer cells (diameter = 60 mm) were placed in a triaxial loading frame. On inundation with distilled water, the specimens were prevented from swelling by the reaction developed in the rigid loading frame. The swelling stresses developed in the specimen (as swelling strains are prevented) were measured using a load cell as a function of time. The swelling stress at equilibrium is defined as swell pressure. The swelling stress of 50B-Ag-K specimen became nearly constant in approximately 15 min, whereas the swelling stress of bentonite specimen needed 44 h to attain constant value.

Results and Discussion

Mechanism of Silver Retention by Kaolinite

Table 2 details the gravimetric weight loss measurements conducted on 1.25 g of 80B-20AgK specimen (constituted by 1.0 g of kaolinite and 0.25 g of silver nitrate) on heating at 400°C for 30 min. According to reaction 3, 0.25 g of silver nitrate salt should experience 0.07 g of weight loss on complete decomposition. The silver nitrate + kaolinite mix experiences weight loss of 0.12 g (Table 2) under the experimental heating conditions; the additional weight loss of 0.05 g experienced by the mix is explained from the results of Kallai (1978). On heating kaolinite-salt mixes at temperatures below 600°C, the kaolinite mineral experiences salt-catalyzed dehydroxylation. The reaction commences with the dehydroxylation of kaolinite; the water liberated during dehydroxylation dissolves the salt particles that further catalyze the dehydroxylation reaction. In line with the observations of Kallai (1978), the additional weight loss of 0.05 g on heating the silver nitrate-kaolinite mix is attributed to the salt-catalyzed dehydroxylation of kaolinite.

Table 2. Weight Loss on Heating Silver Nitrate-Kaolinite Mix

Material	Initial mass (g)	Mass (g) after heating at 400°C	Weight loss (g)
20% silver nitrate + kaolinite mix	1.25 (0.25 g silver nitrate + 1 g kaolinite)	1.13	0.12

Table 3. Amount of Silver Retained by Kaolinite on Heating 20% Silver Nitrate-Kaolinite Mix

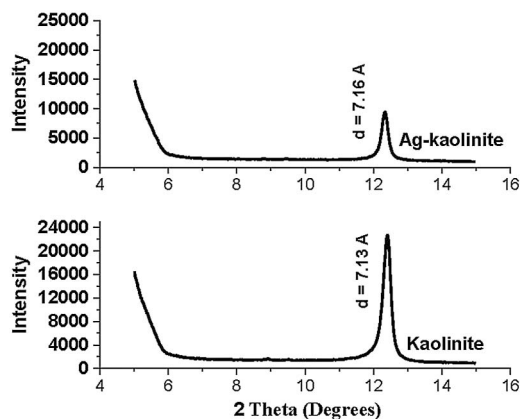
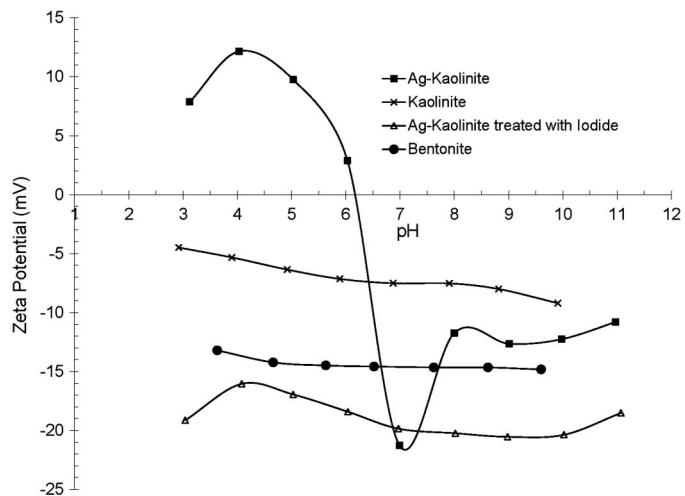
Total silver retained by kaolinite (mg/g)	Nonexchangeable silver (mg/g)	Exchangeable silver (mg/g)
150 (139)	135 (125)	15 (14)

Note: Values in parentheses are in terms of meq/100 g.

Reaction 3 predicts that decomposition of 0.25 g of silver nitrate in the 20% silver nitrate-kaolinite mix should yield 0.18 g of AgO (or 160 mg of nonexchangeable silver) per g of kaolinite. Table 3 provides the amount of silver retained by the kaolinite specimen on heating the 20% silver nitrate-80% kaolinite mix at 400°C for 30 min. Heating the mix caused 150 mg of silver to be retained per g of kaolinite; further, 15 mg (of the 150 mg of silver) occurred in the exchangeable form (on the basis of ammonium acetate extraction results, Table 3). Comparing the nonexchangeable amounts of silver determined experimentally (135 mg) and predicted from reaction 3 (160 mg) indicates that nearly 85% of silver nitrate in the (20% salt-clay) mix participates in the thermal decomposition reaction.

The size of an AgO molecule is 0.18 nm. XRD patterns of kaolinite and Ag-K specimens were obtained for the 2θ range of 5–15° (Fig. 5). The XRD pattern of the Ag-K specimen shows 001 spacing at 0.716 nm, whereas the corresponding spacing for kaolinite occurs at 0.714 nm. The 001 spacing represents the distance between two unit layers of a clay mineral (van Olphen 1963). Intercalation of an AgO molecule between the unit layers of kaolinite ought to have increased its 001 spacing to 0.894 nm (0.714 nm + 0.18 nm). Therefore, the similar 001 (*c*-axis) spacings of kaolinite and Ag-K specimens imply that the AgO molecules are not intercalated in the interlayer space of kaolinite but are retained on the surface. Combining the results of mass balance calculations, amounts of silver retained by kaolinite, and XRD analysis, shows that on heating a 20% silver nitrate-kaolinite mix, 85% of silver nitrate contained in the mix participates in the thermal decomposition reaction with the reactions product being retained on the clay surface.

Fig. 6 plots the zeta potential of kaolinite and Ag-K specimens as a function of suspension pH. Kaolinite is characterized by negative zeta potential of –4.5 to –9.9 millivolts over the pH range of 2.9 to 9.9 and, consequently, does not exhibit an isoelectric point (IEP). The pH of kaolinite suspensions were artificially varied between 2.9 and 9.9 by adding dilute nitric acid or sodium hydroxide

**Fig. 5.** XRD patterns of kaolinite and Ag-kaolinite for the 2θ range of 5–15°**Fig. 6.** Zeta potential measurements as function of pH

solutions to examine the zeta potential of the clay over a wide range of pH values. Significant variations exist in the reported zeta potential of kaolinite specimens (Yukselen and Kaya 2003); in the alkaline pH range (10–11), the kaolinite suspensions exhibit zeta potential of –30 to –85 millivolts and, in the acid (2–3) pH range, –25 to 10 mV. In the present study, the kaolinite suspension exhibits a lower range of zeta potentials compared with values reported in the literature, indicating smaller diffuse ion layer formation (Yukselen and Kaya 2003). On silver retention, the Ag-K specimen exhibits IEP at a pH of 6.2. The IEP of a mineral is the pH at which zeta potential is zero (Pansu and Gautheyrou 2006). The results imply that retention of silver as AgO and exchangeable silver imposes a net positive charge on the clay surface at pH < 6.2. The Ag-K suspension (solids: water ratio, 1:2.5) is characterized by an alkaline pH of 9.0, apparently from hydrolysis of retained AgO as per reaction 1. The IEP value (6.2) of the Ag-K suspension implies that the material is characterized by a net negative charge at pH 9.0. Theoretically, the negative charge of the Ag-K specimen at pH 9 should cause it to repel iodide ions. However, the next section shows that iodide ions are retained by formation of the AgI phase (reaction 2), implying that iodide retention by Ag-K is independent of in situ pH conditions.

Iodide Retention Studies

Tests with Ag-Kaolinite

Fig. 7 plots the kinetics of iodide sorption using an Ag-K specimen from a 1,000 mg/L iodide solution. The pH of 1,000 mg/L of the iodide solution is 5.3. Addition of 0.5 g of a Ag-K specimen to (100 ml) iodide solution increased its pH to between 9 and 10. The plot shows that iodide removal is a very rapid process and is complete in approximately 5 min. At equilibrium, the Ag-K specimen exhibits 74% iodide removal, whereas the 90B-10AgK and 80B-20AgK specimens remove 7 and 13% of the initially present iodide ions.

Fig. 8 plots iodide sorption by Ag-K specimens as a function of initial iodide concentration. Iodide sorption increases rapidly up to initial concentrations of 750 mg/L and thereafter tends to attain equilibrium. At equilibrium, the Ag-K specimen sorbs approximately 59 meq/100 g of iodide ions. The Ag-K specimen is characterized by 125 meq/100 g of nonexchangeable silver (in the form of AgO) and 14 meq/100 g of exchangeable silver (Table 3).

Measurements of solution pH during the iodide sorption experiments revealed that the acidic sodium iodide solutions (pH 5 to

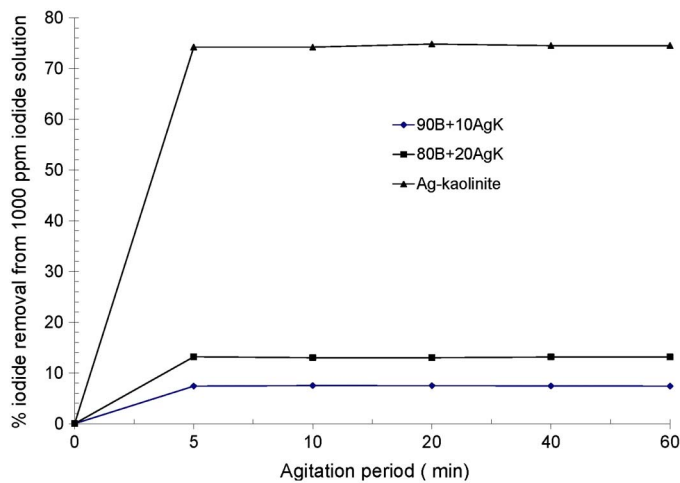


Fig. 7. Kinetics of iodide removal from 1,000 mg/L iodide solution

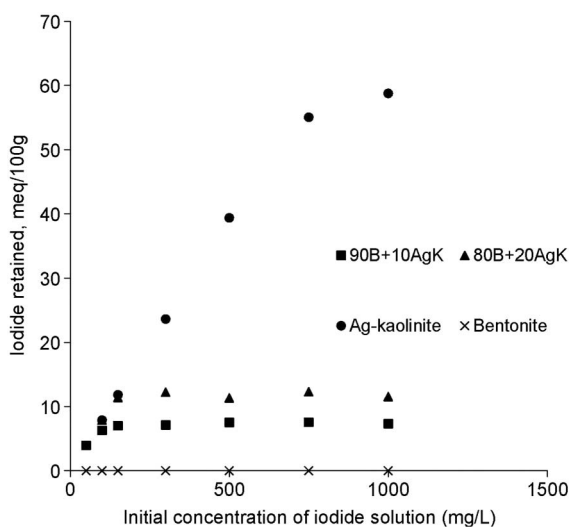


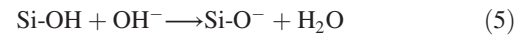
Fig. 8. Iodide sorption by Ag-kaolinite as a function of initial iodide concentration

5.67) were rendered alkaline (pH 9.11 to 9.48) through equilibration with the Ag-K specimen (Table 4). The alkaline pH of the iodide solutions on equilibration of the Ag-K specimen is attributed to the occurrence of hydrolysis and exchange reactions. The hydrolysis reaction is visualized to occur first; the AgO retained on the kaolinite surface hydrolyze (as per reaction 1) on contact with the aqueous solution to form insoluble AgOH and OH⁻ ions. To examine the hypotheses for the occurrence of hydrolysis at contact

Table 4. pH of Iodide Solution on Equilibration with Ag-Kaolinite Specimen

Iodide solution concentration (mg/L)	pH of solution before equilibration	pH of solution after equilibration
88	4.98	9.11
226	5.05	9.36
469	5.14	9.48
759	5.35	9.45
998	5.67	9.31

of Ag-kaolinite with the aqueous medium, the Ag-K specimen was equilibrated with distilled water (solids:solution ratio = 1:100); the pH of the suspension (measured as a function of time) increased almost immediately (1 min) to 8.9 on contact with distilled water (Fig. 9). The subsequent gradual decrease in the pH of the Ag-K-distilled water suspension from 8.9 to 8.29 (after 150 min of agitation) is attributed to dehydroxylation of silanol (Si-OH) groups at particle edges according to the reaction



Sequent to AgOH formation, iodide ions from the salt solution are postulated to replace the hydroxyl groups of AgOH (as per reaction 2) that result in the formation of the AgI phase and release of additional OH⁻ ions to the solution. Evidence for such a chemical reaction is provided by the XRD pattern of the Ag-K specimen equilibrated with a 1,000 mg/L sodium iodide solution (Fig. 10) that shows a peak at 0.375 nm characteristic of AgI phase.

Fig. 9 traced the increase in the pH of distilled water on contact with the Ag-K specimen. The pH of distilled water increased to 8.9 almost immediately. Comparing the relative rates of iodide retention (Fig. 7) and hydrolysis of Ag-K specimen (Fig. 9), the slower OH-I exchange appears to be the rate determining step in the iodide retention process.

Fig. 6 includes the zeta potential of Ag-K specimen contacted with a 0.01 M sodium iodide solution whose pH was varied from 3–11 during the course of the experiment. The plot in Fig. 6 shows that on exposure to the iodide solution, the Ag-K specimen acquires a larger negative zeta potential than the unexposed Ag-K specimen at most pH values (except pH 7). Iodide sorption alters the surface charge on the Ag-K specimen such that it exhibits a negative zeta potential even in the acid pH range.

Fig. 11 plots the iodide leached from the iodide sorbed Ag-K specimen as a function of solution pH. Forty eight mg of iodide were adsorbed per g of Ag-K specimen on equilibrating the clay with a 500 mg/L iodide solution. On agitation of the iodide sorbed Ag-K specimen, with strongly acidic (pH = 2.5) to strongly alkaline (pH = 12.5) solutions, a negligible (0.06 mg) amount of iodide was released by the specimen, indicating that iodide retention by the Ag-K specimen is practically irreversible even under extreme pH conditions.

Tests with Bentonite-Ag-K Specimens

Fig. 7 includes the retention from a 1,000 mg/L iodide solution using 80B-20AgK and 90B-10AgK specimens. The pH of the iodide solution was not controlled and increased from an initial value of 5.7 to 9.3 at the end of equilibration. Dilution of bentonite with 10 and 20% Ag-K did not affect the rate of iodide retention and the process was completed in 5 min. Fig. 8 shows the results of the iodide sorption experiments conducted with B, 80B-20AgK, and 90B-10AgK specimens. Bentonite does not adsorb iodide ions (Fig. 8) as they are repulsed by the negatively charged clay surface (Mitchell 1993; van Olphen 1963). Fig. 6 includes the variations in the zeta potential of bentonite as a function of suspension pH and the expansive clay exhibits zeta potential values ranging from -13 millivolts at pH 3.6 to -14.8 millivolts at pH 9.6; the net negative charge impairs iodide retention by these clay particles. Bentonite is observed to exhibit larger negative zeta potential than kaolinite at common pH (Fig. 6).

The Ag-K specimen shows strong affinity for iodide retention for reasons elaborated previously. The 90B-10AgK specimen shows iodide sorption capacity of approximately 6 meq/100g, whereas the 80B-20AgK specimen shows iodide retention capacity of approximately 12 meq/100 g (Fig. 8). The B-Ag-K specimens attain sorption equilibrium at an iodide concentration of 300 mg/L,

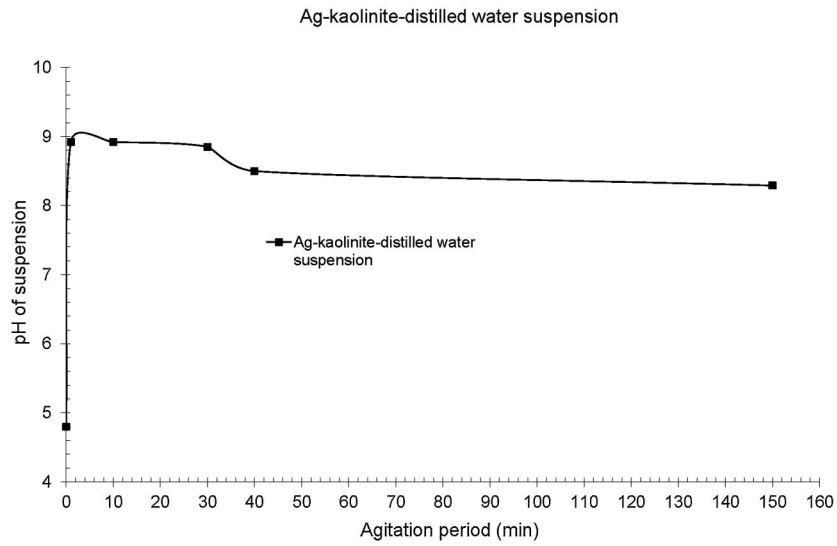


Fig. 9. pH variation of Ag-kaolinite suspension over time

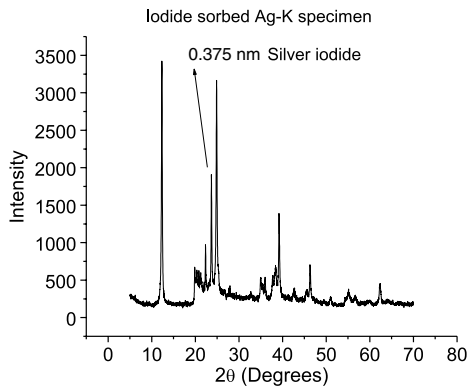


Fig. 10. XRD pattern of Ag-kaolinite equilibrated with 1,000 mg/L iodide solution

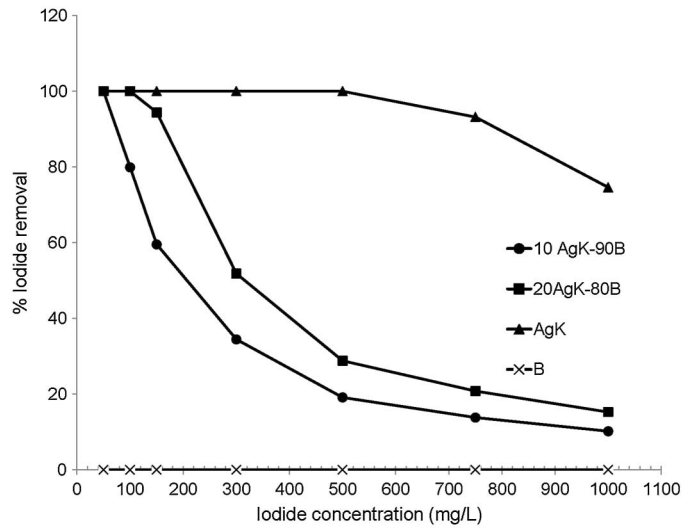


Fig. 12. Percent iodide removal plots

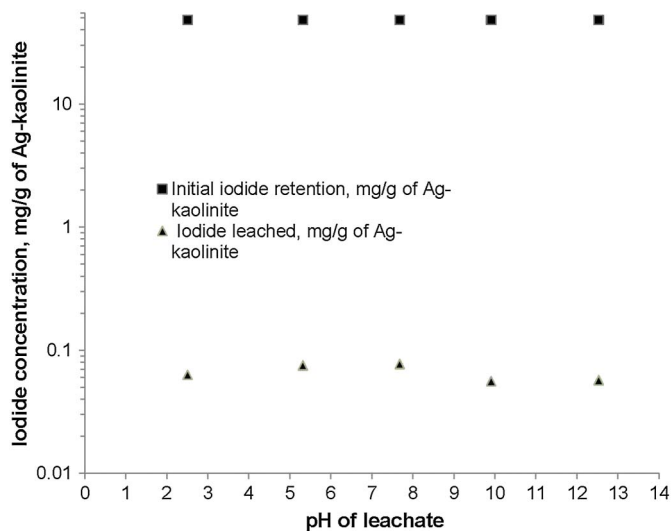


Fig. 11. Iodide leached from Ag-kaolinite as a function of solution pH

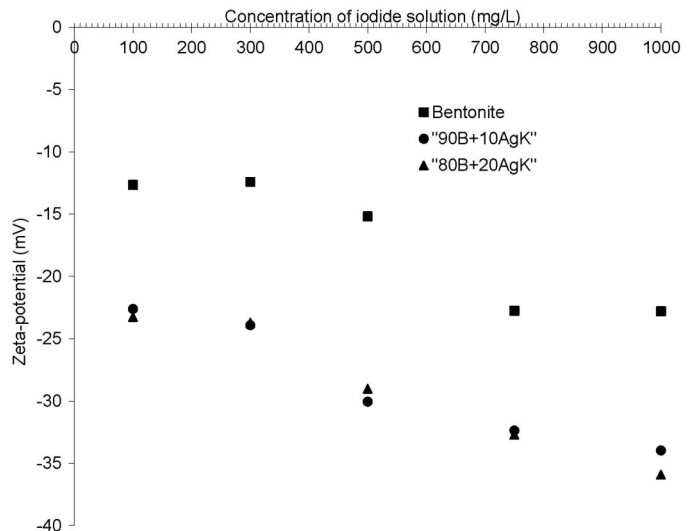


Fig. 13. Zeta potential variation as a function of iodide concentration

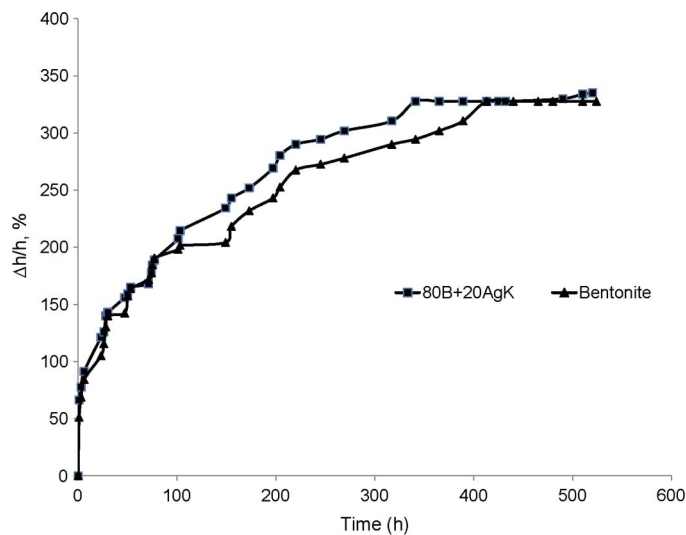


Fig. 14. Time-percent swell plots for compacted bentonite and 80 B-20AgK specimens

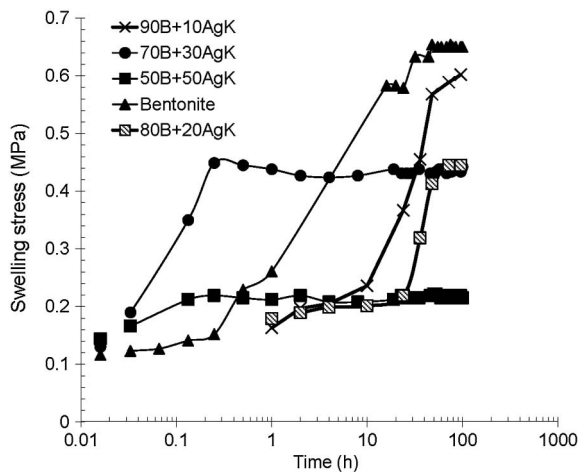


Fig. 15. Time-swelling stress plots

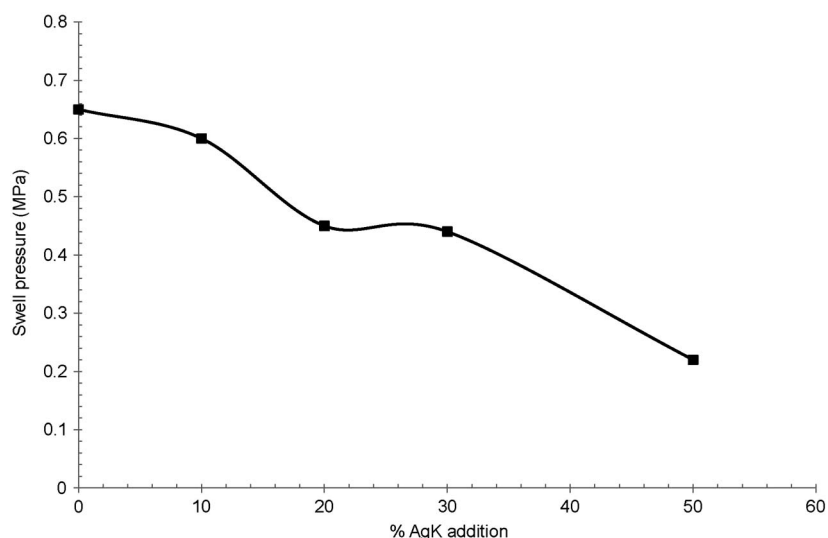


Fig. 16. Influence of Ag-K dilution on swell pressure of bentonite

which is lower than the value observed for Ag-K (750 mg/L, Fig. 8). Fig. 12 plots percent iodide removal as a function of initial iodide concentration. Ag-kaolinite scavenges all iodide ions from solutions containing iodide concentrations of up to 500 mg/L. The 90B-10AgK and 80B-20AgK specimens exhibit 100% removal up to iodide concentrations of 100 mg/L.

Fig. 13 plots the variations in zeta potential values of B, 80B-20AgK, and 90B-10AgK specimens equilibrated with varying iodide concentrations. The zeta potential of bentonite increases from -12.65 millivolts to -22.8 millivolts with an increase in iodide concentration from 100 to 750 mg/L. On addition of electrolytes, the zeta potential of clay particles is expected to decrease because of a shift of counterions toward the Stern layer when the diffuse ion layer is compressed (van Olphen 1963; Mitchell 1993). The increase in zeta potential in Fig. 13 indicates that the anionic component of the electrolyte (iodide) and not of the cationic component (sodium) has a dominating effect on the zeta potential values and enhances particle repulsion with an increase in the solution's iodide concentration. The 80B-20AgK and 90B-10AgK specimens develop more negative zeta potentials than bentonite at a given iodide concentration, apparently the result of retention of iodide on the particle surface by chemical reaction mechanisms.

Swell Potential and Swell Pressure Measurements

Fig. 14 plots percent swell as function of time for the compacted bentonite and 80B-20AgK specimens. Both specimens were compacted to a dry density of 1.5 Mg/m^3 at 25% water content. The compacted specimens develop similar swell potentials of 330%, indicating that dilution of bentonite with 20% Ag-K does not reduce the swell potential of the expansive clay.

The similar swell potentials developed by bentonite and 80% bentonite +20% Ag-kaolinite suggest that the oedometer swell potential measurements were not sensitive enough to capture the effects of dilution on the swelling ability. Complete development of swelling strains by B and 80B-20AgK specimens needed a relatively long period of 480 to 530 h. Swell pressure developments by similarly compacted B and 80B-20AgK specimens required a relatively shorter period ranging from 15 min to 44 h (Fig. 15). To evaluate the influence of Ag-K dilution on the swelling characteristics of bentonite, the study resorted to swell pressure

measurements. Fig. 16 plots the swell pressure as a function of Ag-K content of the compacted mix. All specimens were compacted to a dry density of 1.5 Mg/m³ at 25% water content. The swell pressure values responded differently and showed reduction on dilution by Ag-K. Ten percent dilution caused an 8% reduction in swell pressure with respect to the undiluted (100% bentonite) specimen. Twenty and 30% dilutions caused 31 to 32% reduction in swell pressure values, whereas 50% dilution caused a 66% reduction (Fig. 16). During reprocessing of used nuclear fuel, volatile iodine species are released as HI and I₂ from the dissolution of the fuel rods in nitric acid (Schmett 2005). Schmett (2005) simulated I₂ generation during dissolution of spent nuclear fuel rods and observed I-129 concentrations ranging from 0.1 to 2 ppm. Superposing the field I-129 concentration levels on I removal efficiency (Fig. 13) suggests that use of a 90B-10AgK mix would suffice to provide 100% removal efficiency. Use of 90B-10AgK also ensures that the swelling characteristics of bentonite are least affected by dilution. The proportional decrease in swell pressure on Ag-K dilution and the enhanced iodide retention results of B-Ag-K specimens bring out that mixing Ag-K with bentonite does not chemically modify the expansive clay; further mixing is only physical in nature with the Ag-K presence contributing to iodide retention.

Conclusions

The results of mass balance calculations, amounts of silver retained by kaolinite, and XRD analysis indicate that heating 20% of silver nitrate-kaolinite mix causes 85% of the silver nitrate contained in the mix to participate in the thermal decomposition reaction with the reactions product being retained on the clay surface. Further, 90% of the retained silver exists as fixed silver (AgO) and the remaining 10% is retained in the exchangeable (Ag⁺) form. Kaolinite does not exhibit an isoelectric point (IEP) over the pH range of 2.9 to 9.9. However, on silver retention, the Ag kaolinite exhibits IEP at pH of 6.2. The iodide retention by Ag-kaolinite is attributed to occurrence of hydrolysis and exchange reactions. On contacting the Ag-kaolinite specimens, the AgO species hydrolyze to form AgOH; iodide ions are retained by replacing the hydroxyl group of AgOH, leading to formation of the AgI phase. The I-OH exchange is the rate determining step in the iodide retention process. The Ag-kaolinite specimens acquire relatively large negative zeta potential values at all experimental pH values (−16 millivolts at pH = 4.1 to −20 millivolts at pH = 9) on iodide retention. The strong negative charge of bentonite excluded iodide retention. Mixing bentonite with 10 and 20% Ag-kaolinite (on a dry mass basis) imparted iodide adsorption capacities of 6 and 12 meq/100 g, respectively. The 90B-10AgK and 80B-20AgK specimens developed more negative zeta potential on iodide retention, indicative of dominance of anionic than cationic effect in the presence of electrolytes. Marginal release of iodide retained by Ag-kaolinite occurred under extreme acidic (pH = 2.5) and alkaline (pH = 12.5) conditions. The swell pressure and the iodide retention results of B-Ag-K specimens showed that mixing Ag-K with bentonite is a physical process and the presence of Ag-K only contributes to iodide retention. Superposing the field I-129 concentration levels on I removal efficiency indicate that use of the 90B-10AgK mix would suffice to provide 100% iodide removal efficiency and ensure that the swelling characteristics of bentonite are least affected by dilution.

References

- Balsley, S. D., Brady, P. V., Krumhansl, J. L., and Anderson, H. L. (1998). "Anion scavengers for low-level radioactive waste repository backfills." *J. Soil Contam.*, 7(2), 125–141.
- Breen, C. (1999). "The characterisation and use of polycation-exchanged bentonites." *Appl. Clay Sci.*, 15(1–2), 187–219.
- Bureau of Indian Standards (BIS). (1980a). "Indian standard methods of tests for soils—Part 3." IS: 2720, *Determination of specific gravity of fine grained soils*, New Delhi, India.
- Bureau of Indian Standards (BIS). (1980 b). "Indian standard methods of tests for soils—Part 7." IS: 2720, *Determination of water content-dry density relation using light compaction*, New Delhi, India.
- Bureau of Indian Standards (BIS). (1985a). "Indian standard methods of tests for soils—Part 4." IS: 2720, *Determination of grain size analysis*, New Delhi, India.
- Bureau of Indian Standards (BIS). (1985b). "Indian standard methods of tests for soils—Part 5." IS: 2720, *Determination of liquid and plastic limits*, New Delhi, India.
- Cotton, F. A., Wilkinson, G., and Gaus, P. L. (1995). *Basic inorganic chemistry*, 3rd ed., Wiley, New York.
- Daniels, E. A., and Rao, S. M. (1983). "Silver sorption by metakaolinite from molten silver nitrate." *Z. Phys. Chem.*, 137(2), 247–254.
- Dultz, S., and Bors, J. (2000). "Organophilic bentonites as adsorbents for radionuclides. II. Chemical and mineralogical properties of HDPy—Montmorillonite." *Appl. Clay Sci.*, 16(1–2), 15–29.
- Hesse, P. R. (1971). *A textbook of soil chemical analysis*, John Murray, London.
- Hossner, L. R. (2002). "Dissolution for total elemental analysis." *Methods of soil analysis part-3 chemical methods*, J. M. Bigham, ed., Soil Science Society of America, Madison, WI, 49–64.
- Inyang, H. I., Bae, S., Mbamalu, G., and Park, S. W. (2007). "Aqueous polymer effects on volumetric swelling of Na-Montmorillonite." *J. Mater. Civ. Eng.*, 84–90.
- Kallai, L. H. (1978). "Reactions of salts with kaolinite at elevated temperatures. I." *Clay Minerals*, 13(2), 221–235.
- Kaufhold, S., Pohlmann-lortz, M., Dohrmann, R., and Nuesch, R. (2007). "About possible upgrade of bentonite with respect to iodide retention capacity." *Appl. Clay Sci.*, 35(2), 39–46.
- Mitchell, J. K. (1993). *Fundamentals of soil behaviour*, Wiley, New York.
- Pansu, M., and Gautheyrou, J. (2006). *Handbook of soil analysis: Mineralogical, organic and inorganic methods*, Springer, New York.
- Pennell, K. D. (2002). "Specific surface area." *Methods of soil analysis part 4: Physical methods*, J. H. Dane, and G. C. Topp, eds., Soil Science Society of America Book Series No. 5, Soil Science Society America, Madison, WI, 295–315.
- Perry, H. R., Green, W. D., and Maloney, O. J. (1999). *Perry's chemical engineers' handbook*, 7th Ed., McGraw Hill, New York.
- Pusch, R. (2008). *Geological storage of radioactive waste*, Springer, Berlin.
- Rao, S. M. (2006). "Identification and classification of expansive soils." *Expansive soils: Recent advances in characterization and treatment*, A. A. Rawas, and M. F. A. Goosen, eds., Taylor and Francis, London, 15–224.
- Riebe, B., Dultz, S., and Bunnenberg, C. (2005). "Temperature effects on iodine adsorption on organo-clay minerals. I. Influence of pretreatment and adsorption temperature." *Appl. Clay Sci.*, 28(1–4), 9–16.
- Sazarashi, M., Ikeda, Y., Seki, R., and Yoshikawa, H. (1994). "Adsorption of I[−] ions on minerals for ¹²⁹I waste management." *J. Nucl. Sci. Technol.*, 31(6), 620–622.
- Schmett, G. T. (2005). "Immobilization of fission iodine by reaction with fullerene containing carbon compounds or insoluble natural organic matter." M.Sc. dissertation, Graduate College, Univ. of Nevada, Las Vegas.
- Toyohara, M., et al. (2000). "Iodine sorption onto mixed solid alumina cement and calcium compounds." *J. Nucl. Sci. Technol.*, 37(11), 970–978.
- van Olphen, H. (1963). *An introduction to clay colloid chemistry*, Wiley, New York.
- Yukselen, Y., and Kaya, A. (2003). "Zeta potential of kaolinite in the presence of alkali, alkaline earth and hydrolyzable metal ions." *Water Soil Air Pollution*, 145(1), 155–168.