

ADSORPTION OF ACID MINE DRAINAGE METALS ON FLY ASH¹

by

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Abstract. Fly ash (FA), fluidized bed ash (FBA), and hydrated fly ash (HFA) were assessed for their sorptive properties of metals from acid mine drainage (AMD). Metals in sulfuric acid solutions at different pH conditions were equilibrated with fly ash for varied detention time. Preferential adsorption studies were conducted with respect to six major metals that were found in AMD: iron, manganese, zinc, aluminum, magnesium, and calcium. Comparison of the three fly ashes indicated that all had excellent sorptive properties. However, in the case of the most acidic solution (pH=1), no significant adsorption occurred. After the solution had dropped below a certain pH, adsorption decreased dramatically and release of metals into solution began. Among the six metals, iron seemed to be preferentially adsorbed on fly ash; the adsorption of calcium was not observed. Results indicated that pH was a very significant factor for the adsorption of metals on the fly ash surface. Data obtained from the use of real AMD samples for fly ash treatment were in agreement with experimental observations. Comparison of fly ash with two clays for sorptive properties revealed that fly ash was the best alternative for treatment of acid mine drainage. Treatment of AMD with clay resulted in solutions of low pH and high concentrations of cations in solution.

Additional Key Words: Adsorption, Fly ash, Metals, Acid mine drainage.

Introduction

Acid mine drainage (AMD) can be defined as the pollution resulting from mining activities involving exposure of pyrite to water and oxygen. It is formed primarily by chemical and biological oxidation of pyrite. The main characteristics of AMD are low pH and elevated concentrations of metals. AMD from abandoned mines is a non-point source pollution, thus it contributes greatly to nearby water quality degradation. Although several methods have been developed for AMD treatment, more research, which considers cost and environmental impact, is needed for achieving optimum solution. Perhaps

one cost effective solution is treatment of AMD with fly ash. Fly ash is a fine particle left during coal combustion; it is recovered by air pollution control equipment, and collected in hoppers. The main hypothesis of this study is that fly ash surface is negatively charged, and will remain that way after its contact with acid mine drainage. To test this hypothesis three different types of fly ash with varying physical and chemical properties were evaluated. The high surface area of fly ash and its negative surface charge should induce cation sorption from AMD.

Preliminary investigation has shown that fly ash is capable of

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neutralizing AMD and adsorbing the metals present in this effluent (Atalay, 1992; Moheeth, 1993; Jackson, 1993). Fly ash has also been used in several adsorption studies involving cations; and many of them reported positive results. The only cation that fly ash was reportedly unable to adsorb efficiently was mercury (Gangoli et al., 1975). Moreover, the extent of adsorption of metal ions on the fly ash surface was substantially reduced when the pH of the final solution was in the acid range (Gangoli et al., 1975). The alkaline nature of fly ash is a major contributing factor in the adsorption of metal ions. For lead, the percentage adsorption on fly ash surface increased in the range between pH 3 to 5. The removal of cadmium by adsorption on fly ash was found to increase with increased pH values from 2 to 8, and was maximum between 7 and 8 (Viraraghavan and Rao, 1991). For zinc, the maximum removal was noted at pH 7.5. Several authors (Singh et al., 1991; Mathur and Rupainwar, 1988; Sen et al., 1987; Panday et al., 1985) have reported the pH at which maximum adsorption of selected metals on fly ash surfaces occurs and the oxides responsible for the adsorption of certain ions. Decreasing trend in adsorption was observed for fly ash at very high pH values where the cations were involved in the formation of soluble hydroxy complexes (Yadava et al., 1987).

The alumina content in fly ash is primarily responsible for the adsorption of anions (Panday et al., 1984; Diamadopoulos et al., 1993; Gangoli et al., 1975). A study in which chemical oxygen demand (COD) removal was attempted with adsorption on fly ash also gave positive results (Pankajavalli et al., 1987). At pH > 2.5 the fly ash surface was found not to favor anion adsorption. The adsorption of anions on fly ash is thought to be governed by diffusion followed by surface compound formation. Viraraghavan and Rao (1991) specified the above theory when they were studying the bonding phenomenon between the alumina sites on fly ash and chromate anion.

Studies of Cr(VI) adsorption on fly ash surface (Panday et al., 1984) showed maximum adsorption at pH 2.

The desorption studies for the same element concluded that the weakly bonded adsorbate ions were removed at acid to neutral pH. In alkaline solutions, the Cr(VI) anion was totally desorbed due to the formation of soluble compounds. Diamadopoulos et al. (1993) observed that the maximum adsorption of As(V) on the fly ash surface occurred at pH 4. The arsenic used in their study was in the form of arsenate, which indicated anionic chemistry.

Materials and Methods

Sample Collection

Both fly ash (FA) and hydrated fly ash (HFA) samples were shipped in plastic containers from Oklahoma Gas and Electric Plant, Muskogee, OK. Fluidized bed ash (FBA) samples were generated at the Shady Point Power Plant, Latimer County, OK and shipped to us in plastic containers by Brazil Creek Minerals, Inc., Fort Smith, AR. Acid mine drainage samples (AMD1) and (AMD2) were collected from abandoned mines, "Mine No 7", at Pittsburgh, OK, and "Red Oak Mine" at Latimer, OK, respectively. The bentonite clay was purchased from Central Bag Company, Kansas City, MO. The kaolinite clay was purchased from The Feldspar Corporation, Edgar, FL.

Sample Preparation

Two sulfuric acid solutions were prepared, one at pH=1 and another at pH=4. The following concentrations of metals were dissolved into the above acid solutions: 500 mg/l Fe, 22 mg/l Mn, 5 mg/l Zn, 400 mg/l Ca, 400 mg/l Mg, and 100 mg/l Al. These concentrations reflected the levels of metal present in the actual AMD1 sample. The ratio between the adsorbent and solution was 2 g of fly ash per 100 ml of synthetic AMD. Chaluvadi (1991) and Moheeth (1993) proposed a ratio of 20 g of fly ash per liter of solution. The order with which the six metals were adsorbed on the fly ash surface under the same conditions was determined through preferential adsorption studies. Equal concentrations of each metal, ranging from 1 mg/l to 5 mg/l, were used in solutions of the same ratio as above: 2 g of fly ash and 100 ml of solution. For the screening test,

Table 1: Experimental variables used for the adsorption and neutralization study.

Property Tested	Control Condition	Materials Tested	Acid Solution Used
Adsorption	Conservative ⁴	FA, FBA, HFA	Mineral plus Acid Solutions of pH 1 and 4
	Nonconservative ⁵	FA, FBA, HFA Kaolinite, Na-Bentonite	Mineral plus Acid Solutions of pH 1 and 4
Adsorption and Desorption Tests	Nonconservative	FA, FBA, HFA Kaolinite, Na-Bentonite	4 Different Mineral plus Acid Solutions, Iron plus Acid Solution
Preferential Adsorption	Nonconservative	FA, FBA, HFA Kaolinite, Na-Bentonite	1, 2, 3, 4, 5 mg/l solutions
Screening test (Neutralization capacity and adsorption ability)	Nonconservative	FA, FBA, HFA Kaolinite, Na-Bentonite	AMD2 sample

actual AMD samples were used. Table 1 presents the different experimental variables used in testing cation adsorption on fly ash.

All of the above tests were performed under two controlled conditions: conservative and nonconservative. According to Corbitt (1990) receiving waters can be classified as conservative or nonconservative systems depending on their confined or unconfined nature. For example, reservoirs or lakes are considered conservative systems whereas rivers or estuaries are nonconservative systems. With this analogy in place, the first controlled condition (Table 1) was designed to simulate a conservative system that holds most of the incoming pollutants. Similarly the second controlled condition simulated a nonconservative system with shorter residence times for the pollutants than the first. In order to simulate a conservative

system, the solution added to each sample was shaken in constant speed undisturbed until the solution reached a stable pH value. This stage was defined to simulate equilibrium condition for the conservative system. Equilibrium in this case was reached in an average of seven days. The nonconservative system was simulated with repeated additions and removals of the same amount of solution at constant time intervals. The time intervals for this case were two days each. All experiments were conducted at room temperature.

After the measured amounts of synthetic acid mine drainage and the fly ash samples had been shaken together in high density polyethylene Erlenmeyer flasks, the solid part of the sample was filtered with Whatman No. 2 filter paper from the solution. The solution was digested with nitric acid using a Tecator Digestion Apparatus. Each digested sample was

⁴Systems with long residence time that reach stable pH values.

⁵Systems with short residence times which do not reach stable pH values.

diluted to 100 ml with double deionized water containing 0.2 % lanthanum oxide. The same digestion method was used to analyze raw samples of fly ash. In the case of solid samples filtration was used to separate the digested solid sample from the leachate. The diluted samples were stored in high-density polyethylene bottles until they were analyzed for metals.

Sample Analysis

Digested samples were analyzed for metals using Buck Scientific Atomic Absorption Spectrophotometer VGP System Model 210. High concentration standard metals (1000 mg/l) were purchased from Fisher Scientific and used to prepare diluted standards for calibration. Nitrous oxide/acetylene flame was used to measure aluminum concentration. All other metals were analyzed with air/acetylene flame. Each metal was analyzed using a different wavelength as suggested by Welz (1985).

Results and Discussion

Adsorption of Cations at Varied pH

Table 2 presents the metal concentrations in fly ash and AMD samples. It is apparent from the data that all three ashes contain high levels of calcium, which came from the coal combustion process. In particular, the calcium content in FBA is more than in FA or HFA. This has a lot to do with the uniqueness of the fluidized bed combustion process which operates at a lower temperature and utilizes lime to strip out sulfur from the coal during combustion. In addition, aluminum, iron, and magnesium are found at elevated levels in all three ashes. The two acid mine drainage samples show different metal compositions. AMD1 contains higher levels of iron, magnesium, and calcium than AMD2. The greatest environmental concern from AMD is the high content of iron, manganese, and perhaps aluminum. The concentration of metals in AMD will vary with rainfall events and seepage.

Table 3 indicates that for the conservative system, where the less acidic, pH=4 solution was used as the titrant, total metal removal was

observed in the system except for calcium and magnesium. However, after a certain volume of the titrant was added, some of the cations began to elute into the solution. The concentration of metals observed after the release was higher than those added, which meant that some of the cations originally present in fly ash were also released. This phenomenon was observed mainly in solutions of pH=1. For this reason, adsorption data which resulted from this solution are not presented in graphical forms.

Figure 1 presents the adsorption pattern for iron in the conservative systems. FBA is the fly ash that adsorbs iron totally on its surface after the 600 ml of synthetic AMD have been added to 10 g of fly ash. FA and HFA also adsorb iron for a range of volumes of synthetic AMD added.

Figure 2 also presents the competitive adsorption of iron on fly ash, but for a nonconservative system. Comparison of iron adsorption under the two systems revealed unique differences. Under the conservative system (Figure 1) each ash adsorbed the iron completely when 400, 500, and 600 ml of the acid were added. Consequently, the concentration of iron in solution decreased from 500 mg/l to 0 mg/l. Increased addition of the acid solution, up to 1100 ml, still showed total adsorption of iron. However, increasing the volume of added solution beyond 1200 ml resulted in decreased adsorption of iron from FA and HFA, but not from FBA. Figure 2 showed that total adsorption occurred when 200 ml of the solution was added as opposed to 400 ml to 600 ml in the conservative system.

However, beyond the addition of 400 ml of the solution, both FA and HFA decreased in their adsorption. This is in contrast to the 1100 ml needed to effect iron adsorption in the conservative system. Moreover, the decrease in adsorption was more gradual in the nonconservative system than in the conservative system. FBA exhibited similar behavior in both systems, which was total adsorption of iron throughout the addition of the pH 4 mineral plus sulfuric acid solution. This observed high adsorption capacity of FBA for iron could be beneficial in the use of this ash for treatment of acid mine drainage.

Table 2: Concentrations of metals in fly ash and AMD samples.

Sample	FA	FBA	HFA	AMD1	AMD2
pH	11.9	12.4	12.0	4.5	4.5
Metals	mg/kg			mg/l	
Mn	170	510	270	23	6.8
Fe	35,000	55,000	28,000	600	185
Zn	180	250	190	7.5	3.8
Al	51,500	12,500	44,000	15	8
Mg	40,000	17,500	47,500	595	55.8
Ca	205,000	295,000	190,000	455	75
Na	7,500	1,000	17,800	-	-
K	2,850	3,250	3,000	35	4.1
Cu	2,200	35	185	0.06	-
Cr	65	50	75	1.8	-
Ni	110	70	100	0.45	-
Pb	68	85	170	0.73	-
Cd	< 2	< 2	< 2	< 0.01	-
Ag	< 30	< 30	< 30	< 0.6	-

For the nonconservative system (Table 3), using the same titrant of pH 4, adsorption of cations except calcium occurred throughout the additions. Initially the metals were removed in large quantities, then the amount removed gradually decreased. At the final stage, the concentration of metals in solution reached the initial concentration and in some cases it was even higher, perhaps due to release of metals initially present in the fly ash.

Table 4 shows that for the conservative system, when the most acidic titrant of pH=1 was used, no discernible adsorption occurred. Actually, after a certain pH, release of metals into solution occurred. However, the amount released from the fly ash as compared to the concentration initially present in the solution was not significant. When the volume of solution that was added was low, the concentration was high. As the volume added was increased, the concentration of metals in the solution

decreased, approaching the initial concentration.

For the nonconservative system using the same titrant at pH 1 (Table 4), adsorption occurred only during the first couple of additions of mineral solutions. During successive additions of a mineral solution at this low pH, the quantity of metals released into the solution was the sum of all metals added with the mineral solution and that which was released from the fly ash. Adsorption virtually ceased when release of metals began. Calcium was the cation that was not adsorbed on any of the adsorbents tested, but it was continuously released into the solution. This is due to the fact that the fly ash used contained lime in amounts of 15 to 20 percent by weight. In the nonconservative systems, for both titrants (see Tables 3 and 4) fly ash seems to have a higher capacity in holding metals adsorbed onto its surface than in conservative systems while there is a

Table 3: Metal adsorption from 10^{-4} M metal plus sulfuric acid solution of pH 4 treated with fly ash.

Metal (Initial Concentration mg/l)	Fly Ash	Conservative (for 10 g of fly ash)			Nonconservative (for 10 g of fly ash and 200 ml/addition)		
		ml added while adsorption lasted	pH range for 100 % adsorp- tion	max mg/kg adsor- bed	addit ion of last adsor ption	pH while adsor ption laste d	max mg/kg adsor- bed
Mn (22)	FA	1900	12-8	2200	4	4.5	12800
	FBA	>2000	12-< 8	>3800	8	6	31400
	HFA	>2000	12- 8	2200	5	6	12800
Fe (500)	FA	>2000	12- 8	55000	8	4.5	51200
	FBA	>2000	12-< 8	>95000	>9	<6	88000
	HFA	>2000	12- 8	55000	>8	<5.5	47800
Zn (5)	FA	>2000	12- 8	275	>9	<4	422
	FBA	>2000	12-< 8	475	7	7.5	410
	HFA	>2000	12- 7.5	855	>8	<5.5	418
Al (100)	FA	>2000	12-<4.5	19000	>9	<4	15800
	FBA	>2000	12- 11	7600	>9	<6	15340
	HFA	>2000	12- 8.5	9500	>8	<5.5	14920
Mg (400)	FA	1700	12- 10	20000	2	7	60
	FBA	>2000	12-10.5	36000	6	8.5	41000
	HFA	950	12- 9	24000	2	8.5	9400
Ca (400)	FA	0	-	0	0	7	800
	FBA	0	-	0	0	12	0
	HFA	0	-	0	1	8.5	400

decreased tendency in adsorbing magnesium .

The adsorption studies were based on the worse case scenario of AMD, i.e., the use of a sulfuric acid solution of pH 1 and high concentration of metals. Figure 3 presents the adsorption of iron on all three ashes tested; FBA1 and FBA2 indicate the use of this ash with synthetic AMD and iron solution, respectively. The results are in agreement with the discussion presented for Figures 1 and 2 in that

FBA is the ash which adsorbed the most iron from the solution. It is apparent that FA and HFA are comparatively poor adsorbents of iron. However, both FBA1 and FBA2 were able to adsorb between 75 and 95 percent of the added iron. This observation was consistent within the range of 140 to 700 mg/l Fe addition. When the concentration of iron in the solution increased to 840 mg/l, the amount adsorbed by FBA1 and FBA2 decreased by 30 and 50 percent (from their highest adsorption), respectively. This implies that the available adsorption

site on the surface of FBA had been exhausted. The adsorption study for iron as a single component in solution provided a unique information. The comparison did not show any obvious

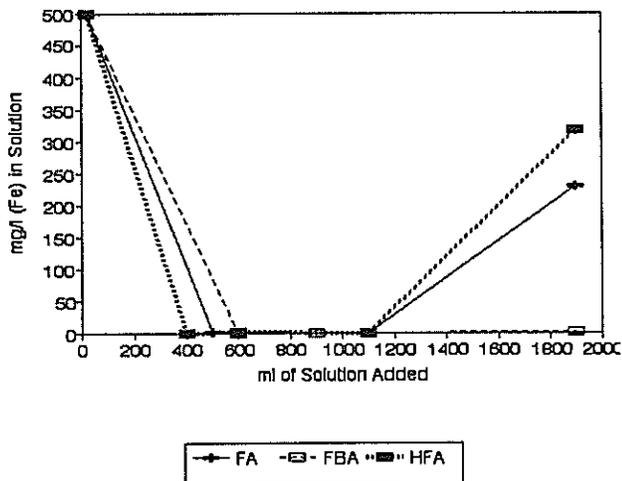


Figure 1: Iron adsorption on fly ash from sulfuric acid and metals solution in conservative systems at pH 4.

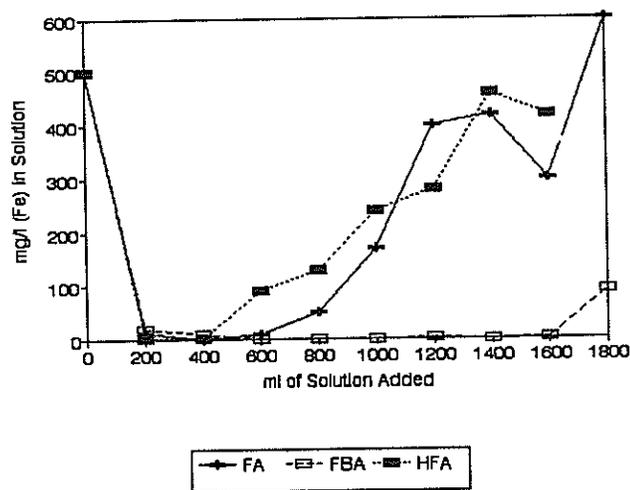


Figure 2: Iron adsorption from pH 4 sulfuric acid and metals solution on fly ash surface in nonconservative systems.

differences in adsorption patterns. This information can lead to the conclusion that iron is adsorbed on specific adsorption sites where the presence of the other cations is not preferred.

This study did not result in any

adsorption or desorption constants because the concentrations were not chosen to produce isotherms. Rather, concentrations were chosen to simulate AMD and to study the patterns of adsorption of cations present in multi-component solutions.

Preferential Adsorption

Preferential adsorption was studied by preparing equal concentrations (1-5 mg/l) of metals in solution and equilibrating them with fly ash. This test was different from any of the above because the initial concentration of metals in solution was much lower than those used in the above studies; and the initial concentration was equal for all six metals (iron, manganese, zinc, aluminum, magnesium, and calcium).

Figure 4 presents the removal of metals using fly ash (FA) during the preferential adsorption tests. Iron, manganese, and magnesium are totally adsorbed by all three types of fly ash. Zinc was partially adsorbed but the adsorption did not show a clear pattern. Calcium and aluminum were released from fly ash in a consistent manner. The presence of varied concentrations of calcium and aluminum in the initial solution did not affect their release from fly ash. Calcium was released in such a manner that its concentration was constant in all samples regardless of its initial concentration in the solution.

Theoretical Adsorption Mechanism

Experimental results showed fly ash to be a suitable adsorbent for the removal of metals from AMD. Surfaces which contain proportions of layer silicates, oxides of iron, aluminum, and manganese are known to have a wide range of trace metal sorption characteristics. Fly ash has such surfaces, moreover, the porous nature of fly ash provides an opportunity for intraparticle transport from bulk to solid-solution interface. The high surface area of fly ash makes many sites available for adsorption interactions.

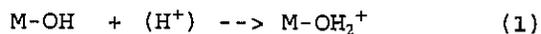
The theory of metal adsorption on fly ash surface is based on the surface charge. For different pH values, oxides at the surface develop

Table 4: Metal adsorption from 0.1 M metal plus sulfuric acid solution of pH 1 titrated with fly ash.

Metal (Initial Concentration mg/l)	Fly Ash	Conservative (10 g of fly ash)		Nonconservative (for 10 g of fly ash and 200 ml/addition)		
		ml added while adsorption lasted	max mg/kg adsorbed	addition where last adsorption occurs	pH while adsorption lasted	max mg/kg adsorbed
Mn (22)	FA	20	44	1	5	440
	FBA	20	44	2	3	860
	HFA	200	440	1	5	440
Fe (500)	FA	600	30000	1	2	10000
	FBA	200	10000	2	2.5	20000
	HFA	500	10000	1	2	12000
Zn (5)	FA	20	10	1	4	40
	FBA	200	100	2	1.8	180
	HFA	300	100	2	2	160
Al (100)	FA	200	200	2	3	4000
	FBA	20	200	0	2.5	0
	HFA	300	2000	2	3	4000
Mg (400)	FA	20	800	0	-	0
	FBA	20	800	1	-	800
	HFA	20	800	0	-	0
Ca (400)	FA	0	0	0	1.8	0
	FBA	0	0	0	12	0
	HFA	0	0	0	2.5	0

different charges. The pH of the system determines whether cationic or anionic adsorption will occur.

In an acidic medium, a positive charge is developed on the oxides of fly ash surfaces. This is because the hydrogen ions are in excess, and they bond with the oxygen on the oxide surface. The bonding that occurs can be described by the following equation:



The resultant positive charge

does not favor the adsorption of positively charged metals on the fly ash surface. In an alkaline medium the oxide surface develops a negative charge. This is because the hydroxide

ions are in higher concentration around the fly ash surface. In this case, the hydroxyl ion has little or no affinity to the oxide surface. However, it serves as a titrator to remove the positive charges from the surface. The reaction can be described by the following equation:



This negatively charged surface favors the adsorption of positively charged metals on the surface. The following exchange reaction describes how the adsorption could take place:

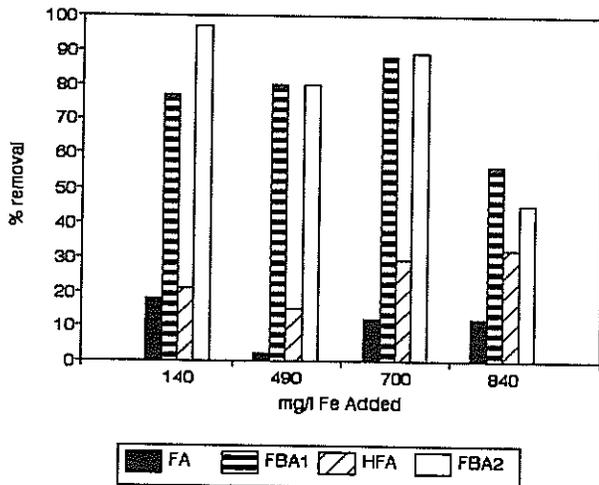
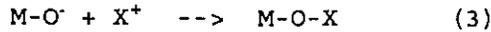


Figure 3: Results for iron adsorption tests using 2 g fly ash samples with 100 ml of metal solutions (Indicators 1 and 2 for FBA samples refer to : 1 mixing with synthetic AMD and 2 mixing with solutions containing only Fe).

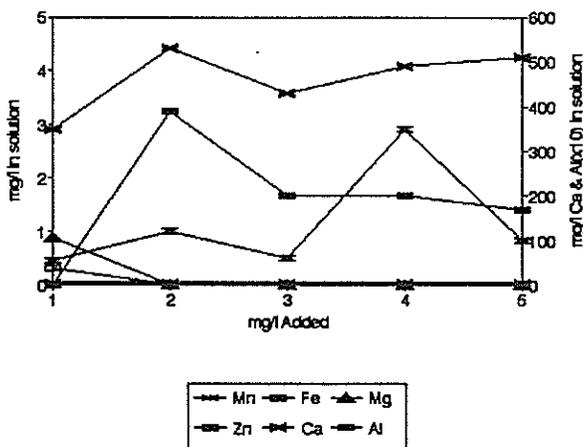
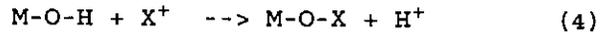


Figure 4: Preferential adsorption of 2 g fly ash samples with 100 ml of metal solution containing equal concentrations of selected metals ranging from 1 to 5 mg/l (Mn, Fe, Mg, Zn, Ca, and Al).

However, there are cases where

adsorption takes place at low pH. This occurs when the surface is neutral and the surface oxygen is bonded with one hydrogen. At relatively low pH, the metal replaces the hydrogen ion on the surface oxide. The exchange reaction that occurs can be described as follows:



This and Wirth, (1977) have discussed in detail the sorptive behavior of trace metals on fly ash. Gangoli et al. (1975) have concurred with the same theory for the removal of heavy metals. Later, many authors (Panday et al., 1984; 1985; Yadava et al., 1987; Singh et al., 1991; Zachara et al., 1992; etc.) used this theory to discuss adsorption on various surfaces.

Using MINTEQA2 to predict precipitation

The geochemical equilibrium model (MINTEQA2) was used to investigate the probability of precipitation of minerals during the sorption process of metals on fly ash surfaces. The input files simulate the metal solutions without the addition of fly ash. However, the pH was set at the same value as that obtained after the addition of fly ash.

Concentrations that were used to prepare the metal solutions were used for a sweep in the MINTEQA2 input file from pH 1 to 12. Results indicated that aluminum precipitated totally at pH 5. Iron and zinc precipitate at pH 8, and magnesium and manganese at pH 10. From tests on preferential adsorption that reached pH values above 12, it could be assumed that aluminum dissolves partially at pH above 12.

Considering the above results from MINTEQA2, and comparing them with the data obtained from the lab, metal removal that occurred at pH below 8 was due to adsorption from solution except for aluminum. At higher pH values, adsorption has to compete with precipitation and the removal could be due to both processes.

Removal of Metals from AMD Using Fly Ash and Clay

Unfortunately, there were two pages that were not scanned and the original is not available to be added here.

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