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Neutralization of an extremely acidic sludge and stabilization of heavy metals in flyash aggregates

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Abstract

An extremely acidic, heavy metal-rich sludge ($pH = -1.2$) was scrubbed with a Class-F fly ash in order to simultaneously neutralize the acidity and stabilize the heavy metals contained in both wastes. This paper outlines the leaching behavior of the aggregate material generated by scrubbing. For proper fly ash/sludge ratios, the fly ash acted as an outstanding neutralizer for the acidic waste. Leaching of heavy metals from the aggregate samples was below the environmental limits within a pH range between 3 and 9. Subsequent washing of the leached aggregate with acidic CALWET solutions did not result in an additional release of heavy metals. It is proposed that coordinative bonding of the metal cations onto neutral surface sites and electrostatic adsorption led to stabilization of the heavy metals within the aggregate structure below hydrolysis pHs.

1. Introduction

The sludge handling and disposal activity are the costliest aspect of industrial wastewater treatment. Up to 60% of the total cost of operating and maintaining wastewater treatment plants is connected with sludge management (Wang and Viraraghavan, 1997; Gupta and Torres, 1998). Therefore, neutralization of industrial wastes and removal of toxic metal ions by low cost adsorbents such as fly ash has been receiving increasing attention (Theis and Wirth, 1977; Talbot et al., 1978; Viraraghavan and Rao, 1991; Jackson et al., 1999; Gupta, 2000; Hequet et al., 2001; Ricou et al., 2001; Lin and Chang, 2001, 2002; Bayat, 2002; Polat et al., 2002a,b). Although the primary components of fly ashes are usually similar (silica, alumina and iron oxides, calcium as lime, anhydrate or gypsum and basic alkali oxides), wide variations in the ratios of these components significantly affect the removal capacity (Corigliano et al., 1997; Hequet et al., 2001). In the adsorption studies where acceptable removal of toxic metals is achieved, removal capacities are usually linked to precipitation of heavy metal hydroxides and formation of calcium silicate hydrates in alkaline fly ash solution (Scheetz and Earle, 1998; Gupta, 2000; Ricou et al., 2001; Lin and Chang, 2001, 2002; Bayat, 2002). Simple precipitation is a reversible process with slight changes in the solution pH and does not satiate environmental concerns. Moreover, fly ash itself contains numerous trace elements in its structure (on the surface, in the aluminosilicate or acid soluble matrix) which could dissolve into solution depending on the solid/liquid ratio, pH, extraction time and temperature (Scheetz and Earle, 1998). Such are the concerns which raise questions about the potential of fly ashes as an adsorbent.

In this work, a Class-F fly ash was used as a scrubber to neutralize an extremely acidic sludge and stabilize the heavy metals contained in both wastes. The fly ash sample was mixed with the acidic sludge to form a paste which was subsequently dried to produce an aggregate product under

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various operational conditions. This paper presents the results of the leaching tests carried out with these aggregates. A three-step stabilization mechanism (surface complexation–electrostatic adsorption–hydrolysis) is proposed to explain the excellent stabilization behavior of the fly ash sample in a wide pH range.

2. Materials

A Class-F fly ash sample from the Rutenberg Power Plant was used in the study. The plant is located in Ashkelon-Israel and burns a South African bituminous coal. The composition of the fly ash sample is presented in Table 1. It is rich in CaO and yields strongly basic solutions in water (over 12 in 1/10 fly ash/water ratio). Zeta potential measurements give a pH_{pzc} of about 5.5 (Fig. 1). The nominal 90% passing size for the fly ash was observed to be 75 μm.

The acidic sludge was obtained from the PAZ-Shmanim recycling plant in Israel, where used motor oils are regenerated by a sulfonic hydrogenation process. Due to the high costs of available treatment methods, a sludge mass amounting to tens of thousands of tons has been kept for more than a decade in large ponds in Ramat Hovav. The sludge is a black, homogeneous organic matter with high viscosity and strong acidity with an apparent pH of −1.2 requiring 19.1 equivalents of NaOH for neutralization (Table 2). It emits dangerous and toxic gases such as SO_2 and SO_3, and great care is required in handling.

Table 1
Chemical composition of the South African fly ash sample

Major components (%)		Trace elements (ppm)			
SiO_2	40.9	Ba	2500	Co	40
Al_2O_3	31.4	Mn	340	Mo	20
CaO	8.4	B	240	Be	6
Fe_2O_3	3.1	Cr	160	As	2
MgO	2.5	V	160	Cd	0.5
P_2O_5	2.0	Ni	135	Ag	0.5
TiO_2	1.8	Zn	110	Hg	0.3
SO_3	0.4	Pb	110	Sr	NA
Na_2O	<0.1	Cu	60		
K_2O	<0.1				
C	4–5				

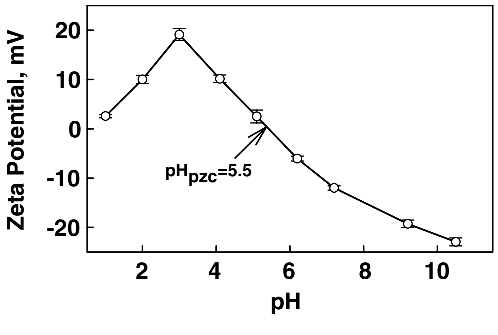

Fig. 1. Zeta potential of the South African fly ash sample as a function of pH (error bars show 95% confidence intervals for five different readings at each point).

Table 2
Chemical composition of the PAZ acidic sludge

Elements (ppm)		Elements (ppm)	
S	186,989	Ni	3.7
Fe	540	Zn	1.7
Ca	50	P	2.0
Si	44	Pb	1.0
Na	11	Sr	0.61
Mg	9.1	V	0.27
Cr	8.9	As	0.26
Cu	6.0	Co	0.20
Al	4.1	Ba	0.14
K	3.7	Cd	0.04
Mn	3.3	Be	0.02

In this article, the following abbreviations will be used to prevent repetitive wording: FA (fly ash), PAZ (PAZ sludge), AP (aggregate product) and W (water).

3. Methodology

The general experimental flow sheet is given in Fig. 2. The acidic sludge was mixed with the fly ash under different operational conditions, such as FA/PAZ and W/PAZ ratios. Representative 10-g samples were obtained from the resulting paste. These samples, dried under ambient conditions for different length of times, formed aggregates structures. The dried aggregate product consisted of nuggest approximately 1 cm in size, but its primary size distribution was similar to that of the original fly ash sample. Kinetic leaching tests were carried out with these aggregate samples in an AP/W ratio of 1/10 (kg/L) up to 90 days in polyethylene bottles. The leachates were analyzed periodically using a different bottle for each sampling time to prevent accumulative error. Each leach-sample was filtered using 0.45 membrane filters, checked for pH and stored for analysis in an ICP-AES. Selected samples were dried following filtration after the 90-day leaching period and were subjected to further leaching in acidic solutions using the CALWET procedure. The CALWET procedure is a standard test to determine the constituents in a solid waste that could potentially leach into groundwater (CALWET, 1991, 2001) and defines threshold leaching criteria for each element (Soluble Threshold Limit Concentration – STLC). A list of STLC values for primary pollutant trace elements is given in the first two column of Table 3. In accordance with the California Code of Regulations (CCR, 1985), the filtered–dried aggregate samples were ground to a fine powder using a mortar, and a 5-g sample from each was treated with 50 ml of 0.2 M sodium citrate solutions (pH 5.0) in polyethylene bottles for 48 h at 25 °C using an orbital shaker. The procedure was repeated for a blank sample without aggregate to provide background for the ICP-AES analyses.

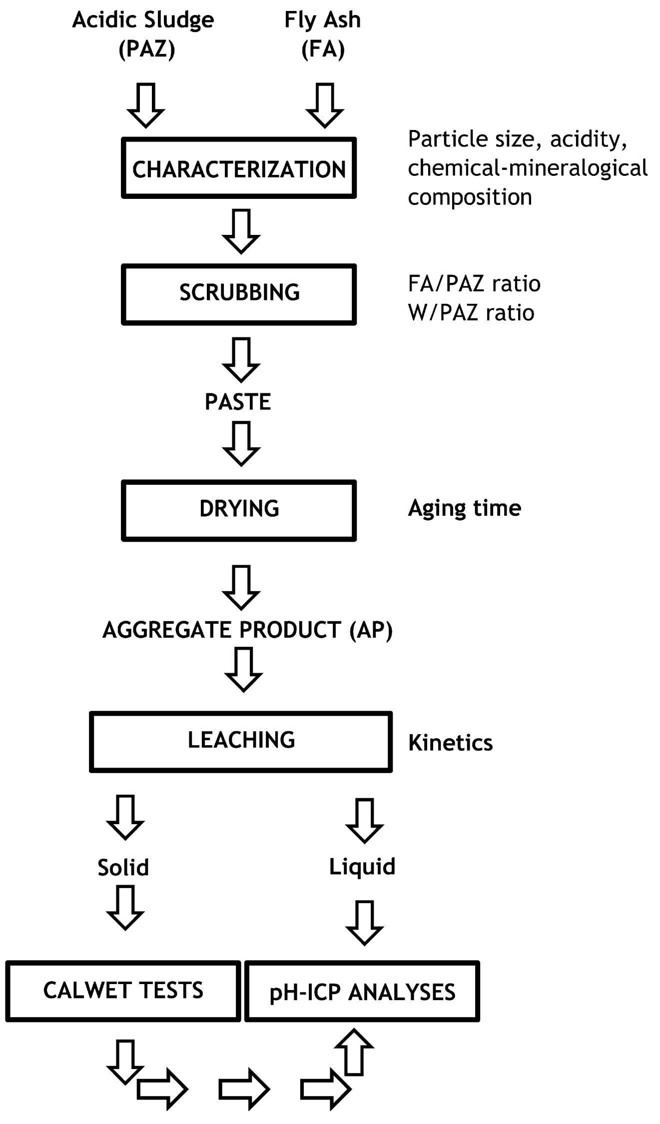

Fig. 2. General flowsheet used in the test work.

4. Results and discussion

4.1. Leaching tests

4.1.1. Effect of FA/PAZ ratio

The fly ash and the sludge were mixed in the reactor for 20 min at FA/PAZ mass ratios of 2, 4, 6 and 8. The paste generated was aged for 3 days in ambient conditions. The dry aggregate was subjected to kinetic leaching tests at an AP/W ratio of 1/10. The amounts of metals in the leach solution (expressed in mg/L) are presented in Fig. 3 for two major elements (Fe and Al) and four trace elements (Co, Cu, Ni and Zn) for leaching times up to 90 days. Although the solutions were analyzed for 16 elements, the discussion in this part will be limited to the above six metals for sake of brevity. A summary for all 16 elements is presented in Table 3.

The top graph in Fig. 3 shows that the pH increases over time and levels off after 90 days at different values depend-

Table 3
The CALWET–STLC values and the metal concentrations after 90 days of leaching in water and after subsequent leaching in CALWET solutions (FA/PAZ: 6, W/PAZ: 2; Aging time: 30 days)

Element	STLC (mg/L)	Metal in water after 90 days (mg/L)	Metal in CALWET solutions after 48 h (mg/L)	% of STLC
Ag	5	0.002	0.013	0.3
As	5	<0.030	0.590	11.8
Ba	100	0.109	0.738	0.7
Be	0.75	<0.0005	0.086	11.5
Cd	1	<0.001	<0.002	<0.2
Cr	5	0.017	2.250	45.0
Co	80	0.002	0.191	0.2
Cu	25	0.004	0.530	2.2
Mo	350	0.554	0.408	0.1
Ni	20	0.002	0.322	1.6
Pb	5	<0.015	0.107	2.1
Sb	15	<0.015	0.047	0.3
Se	1	0.078	0.251	25.1
Tl	7	0.025	<0.100	<1.4
V	24	0.354	3.740	15.6
Zn	250	<0.002	1.001	0.4

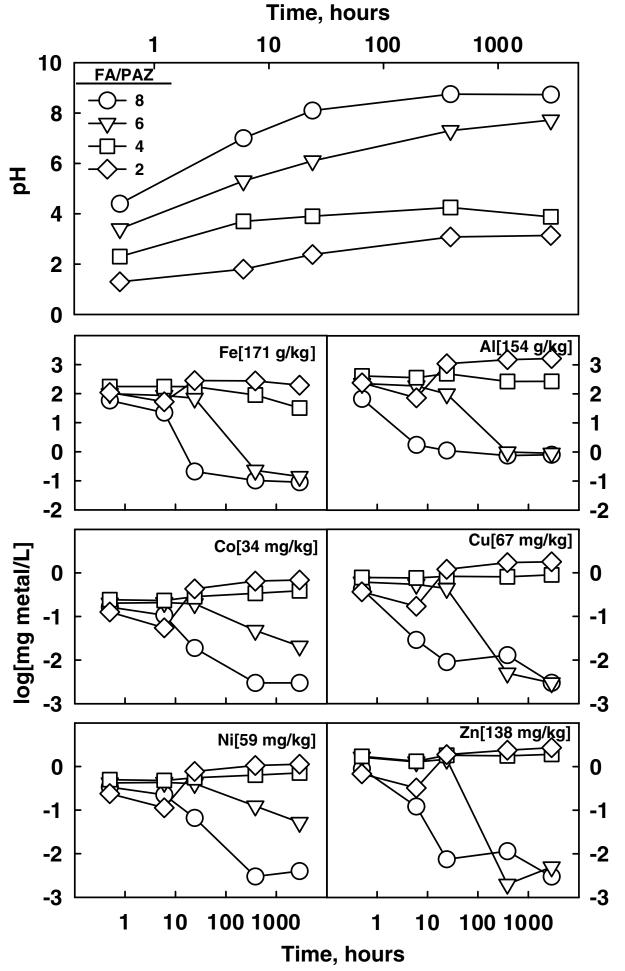

Fig. 3. pH and Fe, Al, Co, Cu, Ni and Zn concentrations of the aggregate solutions as a function of time for different FA/PAZ ratios. The numbers inside each graph give the metal content of 1 kg aggregate (aging time: 3 days; W/PAZ: 0; AP/W: 1/10).

ing on the FA/PAZ ratio. While the final pH was below 3 for a FA/PAZ ratio of 2, it was as high as 9 for a FA/PAZ ratio of 8. This is a consequence of both the strong acidic character of the sludge and the strong neutralization capacity of the fly ash. The amounts of the metals released into solution also varied significantly with the FA/PAZ ratio and time. Both the major and trace elements behaved similarly; their concentrations in solution were higher for a FA/PAZ ratio of 2, increasing with time, but became progressively lower at higher FA/PAZ ratios. For a FA/PAZ ratio of 8, trace metal concentrations in solution were below 0.01 mg/L after 90 days.

4.1.2. *Effect of aging time*

The ash and the sludge were mixed in the reactor for 20 min at a FA/PAZ ratio of 6. The paste generated was dried for 0, 3 and 30 days in air prior to the kinetic leaching tests in an AP/W ratio of 1/10. The results are given in Fig. 4. The pH of the leach solutions showed a slight increase upon aging of the aggregate product. This indicates that a slow secondary neutralization process of the remaining acidic groups of the sludge took place during aging. The heavy metal contents of all the leachates were down to 0.01 mg/L after 90 days for all aging conditions.

4.1.3. *Effect of water/sludge (W/PAZ) ratio*

Prior to mixing with the ash, dilution water was added to sludge at W/PAZ ratios of 0, 1, 2 and 5 by weight. The ash and the sludge were then mixed in the reactor for 20 min at a FA/PAZ ratio of 6. The paste from the reactor was aged for 3 days under ambient conditions prior to the kinetic leaching tests at an AP/W ratio of 1/10. Fig. 5 shows the pH and the Fe, Al, Co, Cu, Ni and Zn concentrations of the leach solutions as a function of time. Addition of water drastically affects the leaching behavior of the aggregate. Initial dilution of the sludge with water accelerated the neutralization of the final aggregate when leached with water reaching pH 8 within the first 1/2 h and stays nearly constant for up to 90 days. The heavy metal concentrations of the solutions after 90 days were very low, below 0.01 mg/L for W/PAZ ratios of 2 and 5. It must be emphasized that the aggregate, containing the added water, was

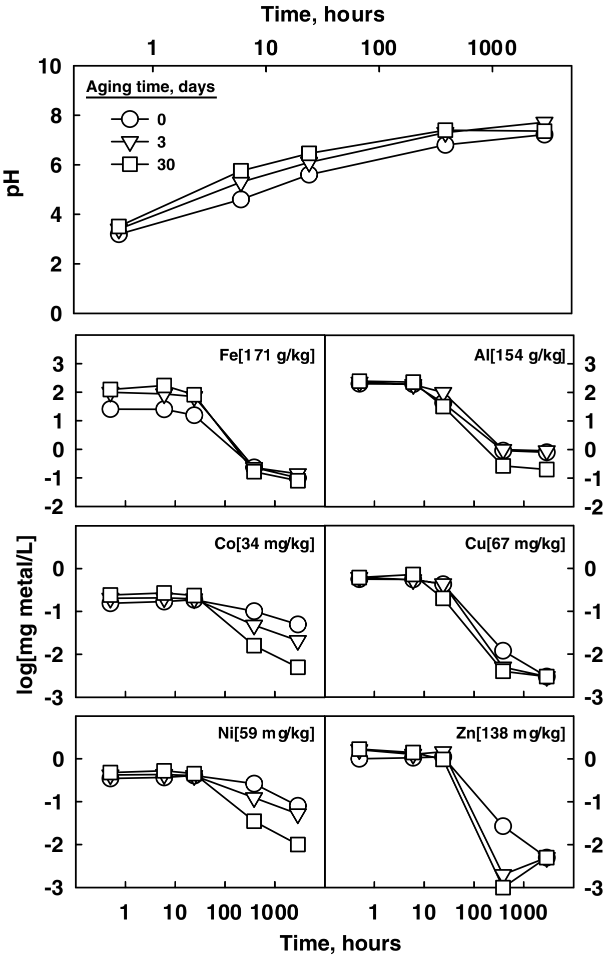

Fig. 4. pH and Fe, Al, Co, Cu, Ni and Zn concentrations of the aggregate solutions as a function of time for different aging times. The numbers inside each graph give the metal content of 1 kg aggregate (FA/PAZ: 6; W/PAZ: 0; AP/W: 1/10).

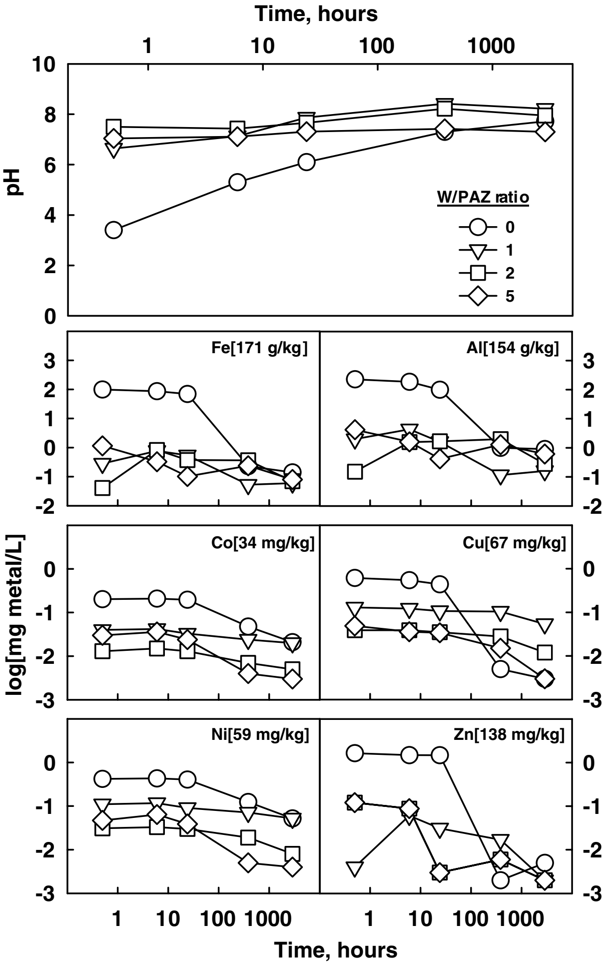

Fig. 5. pH and Fe, Al, Co, Cu, Ni and Zn concentrations of the aggregate solutions as a function of time for different W/PAZ ratios The numbers inside each graph give the metal content of 1 kg aggregate (FA/PAZ: 6; aging time: 3 days; AP/W: 1/10).

aged for 3 days prior to leaching, which exceeds the observed period of 16 h for complete removal of metals from solution in the other tests. It is possible that additional water in the aggregate structure most probably helps the reaction between the ash particles and the sludge by acting as a transport medium.

4.1.4. Effect of externally added trace elements

The aggregate samples prepared at a FA/PAZ ratio of 6 were subjected to leaching tests in solutions that contained an initial 5 mg/L of Co, Cu, Ni and Zn (AP/W ratio of 1/10). The purpose was to observe the adsorptive power of the aggregate samples. The experiment was repeated four times at W/PAZ ratios of 0 and 2 and aging times of 0 and 10 days. The results given in Fig. 6 show that the aggregate is not only capable of retaining metals contained in the fly ash and acidic sludge, but is also able to remove externally introduced metal ions in solution. Metal concentrations in solution progressively decreased and became as low as about 0.01 mg/L after 90 days for all cases. The removal was extremely fast and took place with the first 1/2 h for the aggregate prepared at a W/PAZ ratio of 2 and aged for 10 days.

4.1.5. Additional washing of the leached aggregates with fresh water and acidic CALWET solutions

The aggregate samples that displayed extremely low metal levels in solution (the samples prepared at the FA/PAZ ratio of 6, W/PAZ ratios of 0 and 1 and aged for 30 days) were filtered after 90 days of leaching, dried and placed in fresh water at an AP/W ratio of 1/10. The samples were shaken for 48 h to observe if any metals would be released from the solids into solution. The pH levels of the leach solutions were measured to be around 8 during throughout this period. Fig. 7 presents the combined data both for the initial of 90-day leaching period and for the additional 48-h washing period for Co, Cu, Ni and Zn. It can be seen that no significant leaching of the metals into the fresh solutions takes place during the 48-h washing period in any of the cases tested.

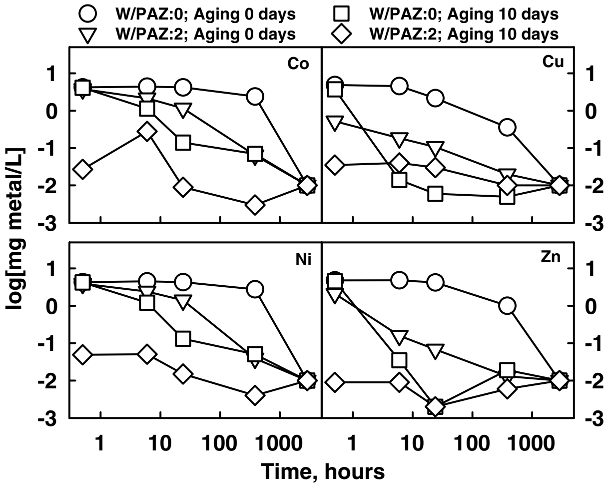

Fig. 6. Co, Cu, Ni and Zn concentrations in leach solutions which contain an initial metal concentration of 5 mg/L for each metal (FA/PAZ: 6).

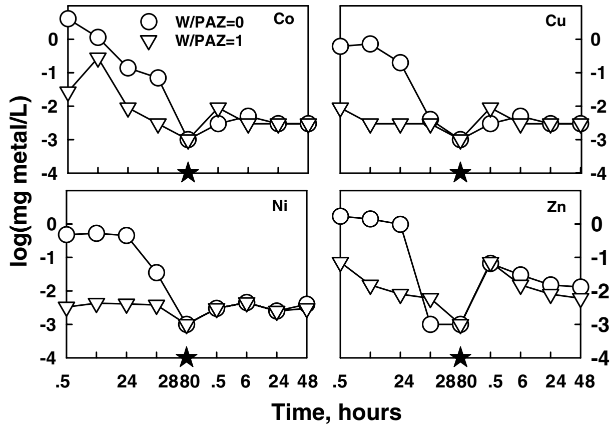

Fig. 7. Additional washing of the aggregate with fresh water for 48 h after leaching 90 days. The stars on the time axis indicate the point where the leach solutions were filtered and the dried solids were placed in fresh water (FA/PAZ: 6; W/PAZ: 0 and 1; aging time: 30 days).

In another set of tests, the aggregate sample prepared at a FA/PAZ ratio of 6, W/PAZ ratio of 2 and aged for 30 days was filtered after 90 days of leaching. The amounts of metals in the leach solution are given in the third column of Table 3 for 16 heavy metals. The solids were dried and subjected to subsequent leaching for 48 h using acidic CALWET solutions. The next column in Table 3 gives the solution metal concentrations following the CALWET leaching for 16 heavy meals. The last column in the table presents the percentage of the STLC values in the leach solutions for each metal for comparison. The table clearly demonstrates that the metal concentrations in the solutions were below the STLC values for all the metals, and a large number of metals (Ag, Ba, Cd, Co, Mo, Sb and Zn) did not reach 1% of the STLC values. The respective percentages of the STLC concentrations were 0.2, 2.2, 1.6 and 0.4 for Co, Cu, Ni and Zn.

4.2. Mechanism of heavy metal removal

Various studies have suggested physical adsorption of metals onto fly ash surfaces to explain the adsorptive behavior of fly ash (Wang and Viraraghavan, 1997; Hequet et al., 2001; Bayat, 2002). Kanungo and Mohapatra (2000) propose a two-step hydrolysis process to explain the decrease of metal ion concentration in solution and relate it to the solubility constants. Such an explanation implies that metal removal should show sharp variations around the hydrolysis pH values. Calculations according to equilibrium thermodynamic data from Stumm and Morgan (1996) showed that Co(II), Cu(II), Ni(II) and Zn(II), in contact with their hydroxides, give the respective secondary hydrolysis pH values of 8.2, 6.1, 8.0 and 8.0 for the formation of $Me(OH)_{2(s)}$. Although some $MeOH^-$ species would form immediately before the secondary hydrolysis pHs, the dominant metal species are Me^{2+}. The inclusion of Ca^{2+} and SO_4^{2-} ions into calculations (which are present in the fly ash-PAZ aggregates in large amounts) did not result in significant changes in the hydrolysis pHs.

Solution concentrations of Co, Cu, Ni and Zn from all of the leaching tests carried out in this work are presented collectively in Fig. 8 as a function of pH. The data for leaching times of 16 days or longer have been used to ensure equilibrium conditions, and the CALWET–STLC values are also included in the figure for comparison. Considering the profiles presented, the data show that metal concentrations, which are well below the CALWET limits at pH 3, begin to decrease further after this pH value and there is almost a 100-fold decrease until a pH of 6 is reached. It is apparent that a simple hydrolysis process cannot explain such behavior since the cationic forms of Co, Cu, N, and Zn would be dominant within this pH range. Moreover, since Co, Cu, Ni and Zn are in cationic forms at pH values below pH_{pzc} of the fly ash (see Fig. 1), the observed concentration change also cannot be justified by physical adsorption alone.

Therefore, besides physical adsorption and hydrolysis, surface complexation of the metal ions on the surface is suggested to explain the observed behavior. The oxide surface complexation model suggests that metal oxide surfaces form coordinative bonds with protons in solution through equations:

$$[\mathrm{S{-}OH_2}]^+ \leftrightarrow [\mathrm{S{-}OH}]^0 + \mathrm{H}^+_{(\mathrm{sol})} \quad K_1(\mathrm{int})^* \tag{1}$$

$$[\mathrm{S{-}OH}]^0 \leftrightarrow [\mathrm{S{=}O}]^- + \mathrm{H}^+_{(\mathrm{sol})} \quad K_2(\mathrm{int})^* \tag{2}$$

where $K_1(\mathrm{int})^*$ and $K_2(\mathrm{int})^*$ are the intrinsic reaction constants. In the case of charged surfaces, the reaction constants $K(\mathrm{int})^*$ should be replaced with $K(\mathrm{app})^*$ such that $K(\mathrm{app})^* = \exp(-F\Psi_0/RT)K(\mathrm{int})^*$. Metal cations may establish bonds with the $[\mathrm{S{-}OH}]^0$ sites on such oxide surfaces according to the reaction:

$$[\mathrm{S{-}OH}]^0 + \mathrm{Me}^{2+}_{(\mathrm{sol})} \rightarrow [\mathrm{S{-}OMe}]^+ + \mathrm{H}^+_{(\mathrm{sol})} \quad K_3(\mathrm{app})^* \tag{3}$$

where $K_3(\mathrm{app})^*$ is the reaction constant for the adsorption process allowing for the electrostatic interaction. The net surface charge, σ, and surface potential, Ψ, can be calculated using the equations:

$$\sigma = \frac{F}{\phi SM}([\mathrm{S{-}OH_2}]^+ + [\mathrm{S{=}O}]^-) \tag{4}$$

$$\sigma = (8RT\varepsilon\varepsilon_0 I)^{1/2} \sinh\left(\frac{zF\Psi}{2RT}\right) \tag{5}$$

In these equations, F is the Faraday's constant, ϕ is the solids concentration, S is the specific surface area, M is the molecular weight of the solids, R is the gas constant, T is the temperature, ε is the dielectric constant for water and ε_0 is the permittivity of the vacuum.

Therefore, if the values of $K_1(\mathrm{int})^*$ and $K_2(\mathrm{int})^*$, $K_3(\mathrm{app})^*$ are known, the above equations can be simultaneously solved to determine the distribution of surface species $[\mathrm{S{=}O}]^-$, $[\mathrm{S{-}OH}]^0$,$[\mathrm{S{-}OH2}]^+$ and $[\mathrm{S{-}OMe}]^+$ as a function of pH since $S_T = [\mathrm{S{=}O}]^- + [\mathrm{S{-}OH}]^0 + [\mathrm{S{-}OH2}]^+$. Some example calculations are presented in Fig. 9 for the sample case of hydrous iron oxide using $\log K_1(\mathrm{int})^* = -7.28$ and $\log K_2(\mathrm{int})^* = -8.93$ for the distribution of surface sites and $\log K_3(\mathrm{int})^*$ values of -0.48, 2.89, 0.37 and 0.99 for the adsorption of Co, Cu, Ni and Zn onto this surface (Dzombak and Morel, 1990). The most important feature of the figure is that the hydrous ferric oxide surface

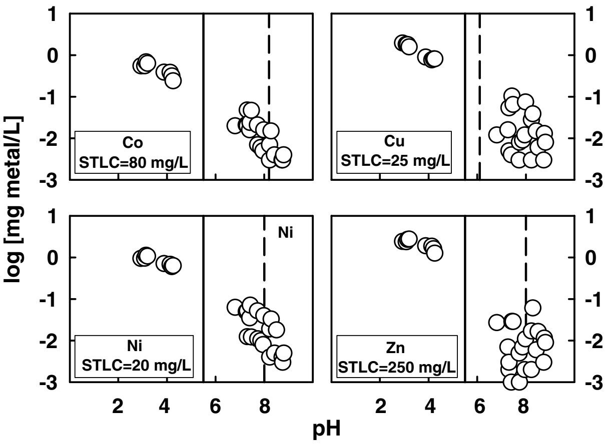

Fig. 8. Collective data for metal concentrations in leach solutions as a function of pH for leaching times of 16 days or longer. The vertical solid line at pH = 5.5 shows the pH_{pzc} of the fly ash sample whereas the dashed vertical line shows the hydrolysis pH for each metal. The CALWET–STLC values are given in the inset boxes.

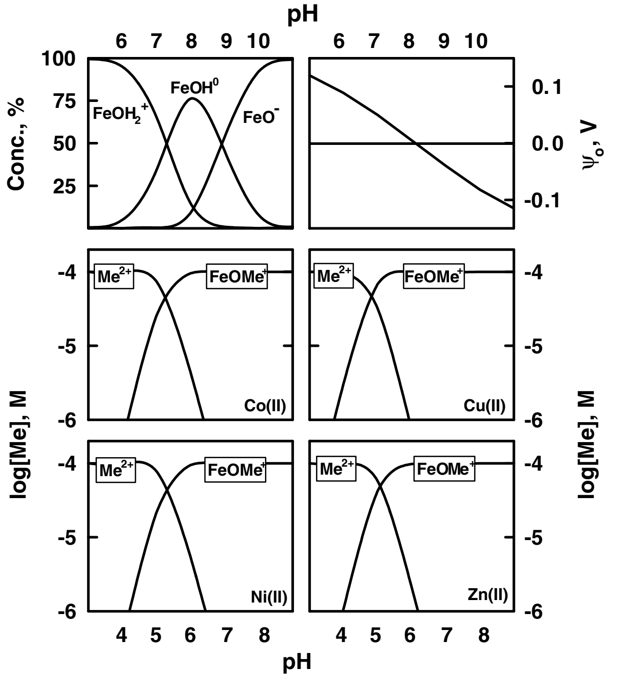

Fig. 9. Distribution of surface species as a function of pH on hydrous iron oxide with the resulting surface potential (top two graphs) and formation of $[\mathrm{Fe{-}OMe}]^+$ complexes on $\mathrm{Fe(OH)_{3(s)}}$ surface by Co, Cu, Ni and Zn ions (bottom graphs) (Total surface $\mathrm{Fe(OH)_{3(s)}}$ concentration is 2×10^{-4} M; Specific surface area of $\mathrm{Fe(OH)_{3(s)}}$ is 600 m^2/g; Total metal concentration for each metal is 10^{-4} M; Electrical double layer model employed is Diffuse EDL).

contains a significant amount of neutral sites within a very wide pH scale even though these sites do not contribute to the net charge. For example, at a pH value of 7 where the surface has a net positive charge, the fraction of neutral surface sites, $[\mathrm{Fe{-}OH}]^0$, is about 35%. In these calculations, only $\mathrm{Me}^{2+}_{(\mathrm{sol})}$ was considered to adsorb onto the hydrous iron oxide surface to form $[\mathrm{Fe{-}OMe}]^+$. It could be seen from the figure that free $\mathrm{Me}^{2+}_{(\mathrm{sol})}$ ions adsorb onto the oxide surface at pH values much lower than the $\mathrm{pH_{pzc}}$ of 8.2 of $\mathrm{Fe(OH)_{3(s)}}$. Indeed, all of the metals in the solution adsorb as $[\mathrm{Fe{-}OMe}]^+$ complexes before a pH of 6 where the net surface charge is positive.

In the case of the fly ash sample used in this study, the $\mathrm{pH_{pzc}}$ is lower, around 5.5 compared to hydrous oxide's 8.2, resulting from the presence of acidic $\mathrm{SiO_2}$ sites due to the high silica content (40.9%). This necessitates that a significant amount of $[\mathrm{S{-}OH}]^0$ neutral surface sites must be present in the system at pH values lower than $\mathrm{pH_{pzc}}$. Such behavior would agree with the data given in Fig. 8 for the fly ash sample. It should be noted that the pH value of 3 at which the metals begin to disappear from the solution in Fig. 8 coincides with the pH where the surface charge on the fly ash begins to decrease (see Fig. 1).

Based on the results presented, it is proposed that the metal removal from solution takes place by three consecutive processes corresponding to different pH regions (Fig. 10). The solution $\mathrm{Me}^{2+}_{(\mathrm{sol})}$ species may adsorb through coordinative bonding onto the neutral $[\mathrm{S{-}OH}]^0$ sites up to or around the $\mathrm{pH_{pzc}}$ of the solid. In the case of the fly ash used in this study, this process takes place in a pH region between 3 and 6 and is responsible for significant decreases in metal concentrations. This is followed by simple electrostatic adsorption of the metal cations, $\mathrm{Me}^{2+}_{(\mathrm{sol})}$, or the first hydroxo-complexes, $\mathrm{MeOH}^{+}_{(\mathrm{sol})}$, after the $\mathrm{pH_{pzc}}$ onto a progressively more negatively charged surface. The final stage is simple precipitation, which forms the $\mathrm{Me(OH)_{2(s)}}$ species after the hydrolysis pH of each specific metal. The coordinative bonding and electrostatic adsorption, which seem to cause significant metal removals from solution in our tests, are more favorable environmentally since they take place at lower solution pH levels and are less sensitive to pH changes in solution compared to hydrolysis.

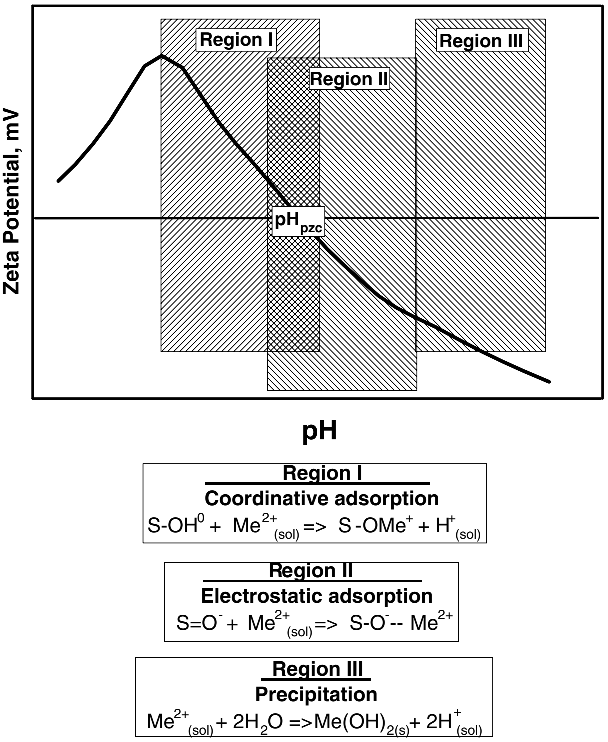

Fig. 10. Proposed mechanism for the removal of heavy metals from the solution by fly ash.

5. Conclusions

The following conclusions could be drawn from this study:

1. South African fly ash is an excellent material for neutralization of extremely acidic organic PAZ Shmanim acidic sludge (pH equivalent of −1.2). The pH of the leach solution of the aggregate produced by mixing the fly ash with the sludge is around 8 for ash/sludge ratios above 4.
2. The aggregate performs extremely well with respect to retaining the metal contained both in the fly ash and in the acidic sludge. Subjecting the aggregate samples to the standard CALWET leaching tests demonstrated that the amounts of leached metals were always below the CALWET limits.
3. The kinetics and the extent of metal removal can be enhanced by optimizing various operational parameters such as diluting the sludge with water and aging the aggregate. Both processes enhance stabilization of heavy metals, most probably by improving the contact between the ash particles and the sludge.
4. It is proposed that heavy metal removal from solution takes place in three consecutive, overlapping pH regions:

   (i) coordinative bonding of the metal cations onto neutral surface sites at pH values below or around $\mathrm{pH_{pzc}}$ of the surface,
   (ii) electrostatic adsorption of the metal cations onto negative surface sites between the $\mathrm{pH_{pzc}}$ and hydrolysis pHs, and
   (iii) precipitation of each metal after its hydrolysis pH.

In the case of the fly ash used in this study, removal of heavy metals to below the environmental limits seem to be predominantly achieved by the collective action of the first two processes.

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