uses lime, cement, fly ash, clay and blast furnace slag to bind the contaminant metals in the cemented matrix (Leist et al., 2003; Singh & Pant, 2006). Soil washing is another common technique for treatment/remediation of soils contaminated with organics and heavy metals. In conventional soil washing process, the excavated soil is vigorously mixed with a solution that leaches contaminants from the waste matrix. Washing usually employs, acids, bases, chelating agents, alcohols or other additives (Griffiths et al., 1995; Sandhya et al., 2006). However, the most efficient washing agents are acids and chelating agents (Neilson et al., 2003; Peters, 1999). Solids content, reaction time and pH are key factors in acid washing (Lo and Chen, 1990). Acid washing involves solubilization of heavy metals in an acid environment as shown in Eq.1 (Lo and Chen, 1990)

$$\text{Sludge-M} + \text{Acid} \longrightarrow \text{Sludge} + \text{M}^{z+} + \text{Acid} \qquad (1)$$

Strong chelating agents such as EDTA, function by complexing heavy metals to form EDTA- metal complexes. Theoretically, one mole EDTA can remove one mole of heavy metals and the reaction can be expressed as in Eq.2 (Lo and Chen, 1990).

$$\text{Sludge-M} + \text{EDTA} \longrightarrow \text{Sludge} + \text{EDTA-Metal Complex} \qquad (2)$$

The present study employs the washing technique to remediate lead contaminated gypsum sludge produced by neutralization of acidific effluent by lime addition in the effluent treatment plant (ETP) of lead-acid storage battery. Chemical forms of the lead contaminants are determined by sequential extraction. Since, acids and chelating agents are recognized to the most effective washing agents, the present study attempts remediation of lead contaminated gypsum sludge by washing the hazardous waste with HCl and EDTA solutions.

MATERIALS AND METHODS

Preparation of Sample

Lead contaminated gypsum sludge was supplied by a lead-acid storage battery industry near Bangalore, India. The sludge sample had average moisture content of 135%. The samples were homogenized and air-dried at 50º C prior to characterization tests. The air-dried mass was pulverized to pass through 1.18 mm Indian Standard sieve and stored in air-tight polythene bags.

Water Leach Test

In the water leach test (ASTM D 3987-85), the air-dried sample is agitated with distilled water for 18 hours (solid to solution ratio = 1:20). After 18 hours, the slurry is filtered and the filtrate is analyzed for dissolved ions such as lead, calcium, magnesium, sodium, potassium, sulfate, chloride and bicarbonate ions using standard test methods.

TCLP Test

Toxicity characteristic leaching procedure (TCLP-Method 1311) test of USEPA, 1996 was performed with air-dried sludge. The mobilization of toxic metals released from wastes is measured using a variety of risk assessment procedures including the Toxicity Characteristic Leaching Procedure (TCLP), among others. The TCLP test is designed to simulate leaching of heavy metals and organics from industrial wastes to be disposed in landfills. The TCLP test measures the possible leachable substances of certain toxic constituents from solid waste under a specified set of laboratory conditions. In the TCLP test, the lead contaminated gypsum sludge was agitated with an acetate buffer (pH= 4.93) solution for 18 hours (solids: solution ratio=1:20). After 18 hours, the slurry is filtered. The leachate is acidified to a pH< 2 (Al-Abed et al., 2006) and analyzed for lead concentration using atomic absorption spectrophotometer.

Estimation of Total Lead Content in Contaminated Gypsum Sludge

Nitric acid digestion was employed to estimate total lead content in the air- dried sludge as per ASTM D 5198-92. In this procedure, 5 g of air-dried sludge was mixed with 25 ml of 1:1 nitric acid: distilled water solution and heated at 90ºC for 2 hours. The mix was cooled to room temperature, filtered and diluted with distilled water to a volume of 200ml. The diluted solution was analyzed for total lead concentration in the sludge sample using atomic absorption spectrophotometer.

Chemical Analysis of Lead Contaminated Gypsum Sludge

The chemical analysis of lead contaminated gypsum sludge was performed using IS; 1288; 1982 procedure. Known mass of sludge (0.2g) is thoroughly mixed for 10 minutes with 50ml of dilute hydrochloric acid (1:250, solid: solution ratio) and filtered. The filtrate was diluted to 200ml. The diluted filtrate was boiled for 2 hours, cooled to room temperature and precipitated with 12% barium chloride solution. The precipitate was filtered and the filter paper was ignited. The residue was weighed and is used to calculate gypsum [(Calcium Sulphate Dihydrate ($CaSO_4.2H_2O$)] present in the sludge sample.

The amounts of silica and acid insolubles present in the sludge were determined by the following procedure. 50 ml of diluted hydrochloric acid was added to 1g of air-dried sludge sample in a porcelain dish and evaporated on a sand bath. Concentrated hydrochloric acid solution was added to wet the residue followed by addition of distilled water. The acidified mix was boiled and filtered. The precipitate contained in filter paper was ignited and weighed to calculate the amount of silica present in the air-dried sludge.

The filtrate from the previous step was used to estimate the amount of iron and aluminium oxides present in sludge sample. The filtrate was acidified with concentrated nitric acid and boiled to ensure oxidation of iron. The boiled solution was cooled to room temperature. Ammonium chloride, methyl red indicator and dilute ammonium hydroxide solution were added to the cooled solution. The solution was once again boiled for a few minutes to facilitate precipitate coagulation. The solution was filtered and the precipitate was washed with hot ammonium nitrate solution until the washings were free from chlorides. The filter paper was ignited and the mass of the residue was used to calculate the amount of iron and aluminium oxides in the sludge sample. The filtrate from previous step was analyzed for dissolved calcium concentration by the EDTA titration method. The calcium concentration in the filtrate was used to calculate the amount of calcium oxide present in the sludge sample.

Sequential Extraction Test

In the sequential extraction process, the sludge was agitated with consecutive extractants for a fixed time interval (Figure1). A solid: liquid ratio of 1:8 was used in the extraction tests. After extraction, the slurry was filtered and the filtrate was acidified (< 2 pH) and analyzed for lead concentration using atomic absorption spectrophotometer. The sludge retained on the filter paper at the end of step 1 was subjected to the next extraction (step 2) using extractant number 2. The procedure outlined in step 1 was repeated till the last extrantant was reached.

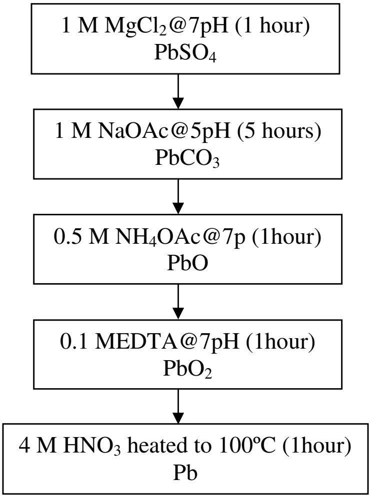

FIG.1 Sequential extraction protocol.

Sludge Washing Experiments

The sludge samples were washed using HCl and EDTA in batch experiments. 0.01 M, 0.1 M and 0.5 M HCl solutions and 0.01 M, 0.1 M and 0.2 M EDTA solutions were used as washing agents in the batch experiments. Preliminary experiments revealed that a solid: liquid ratio of 1:20 was most effective in lead extraction by HCl solutions; comparatively, a solid: liquid ratio of 1:10 was most effective in lead extraction by EDTA solutions. In a typical batch experiment, the sludge was agitated with required concentration of HCl solution (S/L ratio 1:20) or EDTA solution (S/L ratio 1:10) for 18 hours using a mechanical shaker at 120 revolutions/minute. At the end of equilibration, the slurry was filtered and filtrate was acidified and analyzed for lead concentration. Concomitantly residue retained on filter paper was dried at 50ºC and weighed to calculate the amount of sludge dissolution by the washing procedure. The weighed mass was used to calculate the percentage dissolution of sludge by the washing procedure using the formula:

$$\frac{Initialmas\ sofsludge - massofslud\ geafterwas\ hing}{Initialmas\ sofsludge}\times 100\% \tag{3}$$

RESULTS AND DISCUSSION

Chemical & Mineralogical Characterization of Lead Contaminated Gypsum Sludge

Table 1. Chemical Composition of Air-Dried Sludge

Constituent	% Weight
Calcium sulfate dihydrate	90
Silica	0.9
Iron & Aluminium oxide	1.4
Calcium oxide	5.7
Magnesium oxide	2.7
pH	9.01
Total Dissolved Salts (mg/l)	2616

Table 2. Water Leach Test on Air-Dried Sludge

Constituent	Conc. (mg/l)
Lead	0
Sulfate	908
Calcium	720
Magnesium	49
Potassium	2
Sodium	39
Chloride	840
Bicarbonates	58

Table 1 presents chemical compositions of the sludge sample. The sludge is predominantly (90%) constituted by calcium sulfate dihydrate ($CaSO_4.2H_2O$) and lesser amounts of calcium oxide (5.7%), magnesium oxide (2.7%), iron and aluminium oxide (1.4%), and silica (0.9%) respectively. Data in Table 1 also shows that the sludge has an alkaline pH of 9.01. Ordinarily calcium sulfate dihydrate ($CaSO_4.2H_2O$) has slightly acidic pH of 5.7. The alkaline nature of the lead contaminated gypsum sludge arises due to the presence of unreacted lime in the sludge (Table 1). The sludge sample has total dissolved salt concentration of 2616 mg/l that is mainly contributed by calcium, magnesium, potassium, sodium, sulfate, chloride and bicarbonate ions.

Lead Leachability of Contaminated Sludge

Table 3 presents the results of water leachability test, TCLP test and total lead content estimation in the sludge sample. Leaching with distilled water did not extract any lead from the sludge sample. However, the TCLP leachate was characterized by lead concentration of 10 mg/l that exceeds the TCLP limit of 5 mg/l (USEPA, SW 846). Nitric acid digestion of lead contaminated sludge sample revealed total lead content of 2960 mg/ kg of air-dried sludge. The total lead content in the gypsum sludge is less than the prescribed limit (5000 mg/kg) for hazardous wastes (Ministry of Environment and Forests, New Delhi in HWRules-2003). Calculation showed that the acetate buffer (TCLP extraction fluid #1) could only leach 6% of the total lead content from the sludge.

Table 3. Lead Leachability Test Results

Test	Lead Concentration in Leachate mg/l	Lead Concentration in Sludge mg/kg
Water leach test	0	0
TCLP test	10	200
Total lead	----	2960

Fractionation of Lead

Results of the sequential extraction procedure are provided in Table 4. The major fraction of lead in the contaminated sludge occurs in the carbonate form (40%). Oxide forms of lead-lead oxide and lead dioxide constitute 15% and 24% of the total lead in the contaminated sludge. Exchangeable lead (in the form of lead sulfate) is present in minor amount corresponding to 2.8%. The remaining lead is constituted by residual (metallic) lead (14.3%).

Table 4. Sequential Extraction Procedures (Tessier et al., 1979; Clevenger et al., 1991)

Reagent	Time (Hr)	Extracted Form	% of Total Pb
1M $MgCl_2$ (pH 7)	1.0	$PbSO_4$(exchangeable)	2.84
1M NaOAc (pH 5)	5.0	$PbCO_3$(carbonate)	40
0.5 M NH_4OAc (pH 7)	1.0	PbO	15.24
0.1M EDTA (pH 7)	1.0	PbO_2	24.40
4M HNO_3	1.0 (heated)	Pb (residual)	14.26

Acid and EDTA Washing

The results of batch washing experiments are summarized in Table 5. The results in Table 5 show that EDTA is more efficient than HCl in lead extraction. For example 0.01 M EDTA extracts 67% of the total lead in the sludge, while 0.01 M HCl has zero efficiency for lead removal. Like wise 0.1 M EDTA extract 96% of the total lead in the contaminated sludge while 0.1 M HCL extracts only 10% of the available lead in the contaminated sludge. The zero efficiency of 0.01 M HCl in extracting lead is attributed to neutralization of the acid solution by free lime present in the sludge material. Neutralization reaction increases the pH of 0.01 M HCl extractant from an initial value of 1.97 to 8.0 (Table 5); at this altered pH the solubility of lead is minimal (Al-Abed et al., 2006). Examining the efficiency of EDTA solutions it is seen that increasing the strength of EDTA solutions from 0.01M to 0.2 M increases the lead extraction efficiency of the chelating agent from 67% (at 0.01M EDTA) to 100% (at 0.2 M EDTA). Besides increasing molar strength, the final slurry pH values of the EDTA samples may also have influenced the extraction efficiency. The EDTA ligand is most effective in chelating metals from an aqueous system in the pH range of 3 to 6 (Cline & Reed, 1995). The final slurry pH of 0.1 M and 0.2 M EDTA samples correspond to 4.98 and 4.52 that lies in the favorable pH range for chelating heavy metal ions. The final slurry pH value of 0.01 M EDTA sample is 7.98 which does not lie in the favorable pH range.

Table 5. Sludge Washing

Reagent	pH of Reagent	pH of Slurry	Extracted Pb mg/g	% Removal of Pb	% Loss of Solid
0.5 M HCl	0.3	0.48	2.3	77.7	29
0.1 M HCl	1.06	1.6	0.29	9.8	11
0.01 M HCl	1.97	8.0	0.00	0.0	3.5
0.01 M EDTA	---	7.98	1.97	66.6	0.3
0.1 M EDTA	---	4.98	2.83	95.6	5
0.2 M EDTA	---	4.52	2.96	100	17

Table 5 also includes the percentage loss of solids experienced by the sludge sample on extraction with various HCL and EDTA solutions. Data in Table 5 shows that increasing EDTA concentrations 0.01 M to 0.2 M progressively increases the percentage loss of solids from 0.3% to 17%. Although 0.01 M EDTA causes minimum loss of solids, it has the least removal efficiency (67%). 0.1 M EDTA solution has a much higher efficiency of lead removal and also causes lesser dissolution of solids (5%) in comparative to 0.2 M EDTA solution (17%). Based on its high lead removal efficiency and lesser dissolution of solids, 0.1 M EDTA is considered as a most effective washing agent for removing lead from contaminated gypsum sludge.

CONCLUSIONS

The lead contaminated gypsum sludge was characterized for chemical, mineralogical and toxicity properties. Chemical analysis revealed the predominant presence of calcium sulfate dihydrate ($CaSO_4.2H_2O$) in the lead contaminated sludge. TCLP test showed that lead concentration in the leachate exceeded the critical level of 5 mg/l, characterizing it as hazardous waste based on toxicity characteristics. Interestingly, the total lead content in the gypsum sludge (2960 mg/ kg) was below the prescribed limit (5000 mg/kg) for hazardous wastes. Results of the sequential extraction procedure revealed that the major fraction of lead in the contaminated sludge occurs in the carbonate form; lead oxide, lead dioxide, exchangeable lead and residual lead constitute the other forms of lead. The results of washing experiments showed that

EDTA is more efficient than HCl in lead extraction. Further, based on its high lead removal efficiency and lesser dissolution of solids, 0.1 M EDTA is considered as a most effective washing agent for removing lead from contaminated gypsum sludge.

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Synergistic Coupling of ISCO with SEAR and Bioremediation

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ABSTRACT: Treatment of organic contaminants at hazardous waste sites may best be achieved by coupling technologies for improved treatment effectiveness. In particular, sites with high heterogeneity and high contaminant mass may be difficult to treat with a single approach due to difficulties associated with contacting remedial agents with contaminant, the cost of remedial amendments for complete contaminant degradation/removal, and the performance limitations of individual technologies. In situ chemical oxidation (ISCO) is one technology that may be applied prior to, simultaneous with, or after application of other active or passive techniques, in the same or adjacent treatment location. For example, bulk contaminant (e.g., non-aqueous phase liquid, or NAPL) removal, such as provided by surfactant-enhanced aquifer remediation (SEAR), may be necessary prior to ISCO treatment. Passive technologies that provide for a “polishing step”, such as natural attenuation, may be required following source zone removal using ISCO. Laboratory studies were conducted to investigate the important synergies and challenges associated with coupling ISCO with SEAR and with bioprocesses (e.g., natural attenuation). Results demonstrate the promise of these coupling strategies and demonstrate the importance of characterizing reactants and byproducts associated with each individual process in order to exploit positive effects and avoid negative effects in system design.

INTRODUCTION

The subsurface environment is highly complex with media heterogeneities and varied contaminant mass distributions, challenging the applicability of any one individual remediation technology. Also, individual treatment technologies have performance and cost limitations (e.g., transport in different media, amenability of contaminants, contaminant mass or mass distribution, etc.) that may challenge their site-specific applicability. Because of these challenges, the use of coupled remediation technologies to improve treatment and cost effectiveness is receiving increased attention. The focus herein is the coupling of in situ chemical oxidation (ISCO) with surfactant-enhanced aquifer remediation (SEAR) or with bioprocesses. There are both synergies and challenges associated with coupling technologies that must be understood to apply them effectively.

ISCO is a remediation technique where organic contaminants are degraded in place by the delivery of oxidants to the subsurface. Effective treatment relies on effectively distributing/dispersing oxidant and contacting contaminant. Reaction can occur via electron transfer or free radical oxidation, depending on the oxidant employed. Common oxidants include permanganate, persulfate, catalyzed hydrogen peroxide propagations (CHP), and ozone. Byproducts of reaction also depend on the oxidant utilized and may include manganese dioxide solids (with permanganate), gas and heat (with CHP), sulfate (with persulfate), oxygen (CHP and persulfate), and increased dissolved metals (any oxidant). SEAR is the use of surfactants and/or cosolvents (such as water-miscible alcohols, ketones, and sugars) to solubilize or mobilize contaminants via micellar solubilization or due to interfacial tension reductions. Bioremediation is the use of organisms, primarily microorganisms, to degrade contaminants into less toxic forms under either aerobic or anaerobic subsurface conditions. Treatment effectiveness depends on microbial populations present, nutrient availability, moisture, temperature, and pH.

There are two potential approaches for coupling ISCO and SEAR, a co-injection approach where the treatment agents are delivered together (enhanced contaminant dissolution/desorption with concurrent contaminant destruction), and a sequential application of SEAR followed by ISCO to first remove significant contaminant mass followed by a chemical treatment polishing step. Table 1 presents the synergies and challenges associated with coupling ISCO and SEAR described below.

If properly designed, an ISCO/SEAR coupled treatment system can reduce chemical costs for remediation. For example, as more contaminant is removed from a site via SEAR, the remaining mass in the subsurface decreases and less contaminant is removed using a given volume of surfactant/cosolvent due to mass transfer limitations. The cost-benefit (i.e., mass of contaminant removed vs. mass of surfactant/cosolvent introduced) decreases as treatment continues. Treatment of this remaining mass of contaminant may be more cost-effective through a post-SEAR process such as ISCO (Dugan et al., 2007). Furthermore, this sequential approach of SEAR followed by ISCO may improve contact of ISCO oxidants with contaminant remaining post-SEAR. For example, if contaminant is initially present as a NAPL pool at a site where an oxidant is introduced, contact of the oxidant with the contaminant will occur only at the interface of the pool and the treatment solution delivered, then rely on slower contaminant dissolution (which will be enhanced due to destruction of dissolved phase contaminant) (e.g., Schnarr et al. 1998; Hood 2000). If significant NAPL mass is removed via SEAR first, the remaining contaminant may be more evenly distributed in the subsurface, allowing for greater contact of oxidant with contaminant on a mass to mass basis than treating the original NAPL with ISCO alone. An additional advantage is realized in coupling ISCO and SEAR using a co-injection approach. SEAR alone will remove contaminant from the subsurface via enhanced solubilization and/or mobilization, but a post-flush above ground process is necessary to then separate and manage the contaminant. Coupling SEAR with ISCO allows for simultaneous destruction of the contaminant at high concentrations, which increases the efficiency of oxidant use (Li 2004, Zhai et al. 2006).

Table 1. Synergy and Challenges of Coupling ISCO with SEAR

Synergy
Potentially reduced chemical costs if properly designed
Improved contact of oxidant with remaining contaminant post-SEAR (sequential application)
Enhanced contaminant dissolution/desorption concurrent with contaminant destruction (co-injection)
Challenges
Compatibility of oxidants with surfactants/cosolvents to avoid nonproductive oxidant consumption and/or byproduct generation
Compatible *concentrations* of oxidant and surfactant/cosolvent
Managing solids, gas, byproducts, and/or mobilized NAPL
Characterizing remaining contamination post-SEAR (sequential application)

There are challenges, however, in coupling ISCO and SEAR. The primary challenge is in identifying a compatible surfactant/cosolvent and oxidant solution. The ideally compatible solution is one where the surfactant/cosolvent exerts no inherent demand for the oxidant (i.e., nonreactive) that would result in nonproductive oxidant consumption and extensive byproduct generation. This issue of compatibility is important with respect to both sequential application of SEAR and ISCO (where residual surfactant/cosolvent will remain in the subsurface post-SEAR) and co-injection. Laboratory studies conducted to evaluate coupled ISCO and SEAR demonstrate a variety of issues associated with byproduct generation using incompatible surfactant/cosolvent and oxidant mixtures (e.g., Conrad et al. 2002). Another challenge in coupling these technologies relates to the sequential approach of SEAR followed by ISCO. Extensive efforts may be made to characterize the site pre-treatment, however it is essential to characterize the site to an extent post-SEAR so ISCO may be applied appropriately. This involves additional time, effort, and funds, however the cost-benefit can be realized in chemical cost savings.

Typically the coupling of ISCO with *bioprocesses* involves applying ISCO as a first step for significant contaminant mass treatment, followed by biotreatment (enhanced or monitored natural attenuation) as a polishing step for residual contamination. Table 2 presents the synergies and challenges associated with this coupled approach.

If properly designed, an ISCO/bioprocesses coupled approach can lead to reduced chemical costs, particularly at sites with low permeability layers or lenses into which contaminant has diffused and is not readily accessible for oxidation. Rather than continuing to apply oxidants to a site where diffusion processes are significantly slower than oxidation reactions, it is more cost-effective to rely on enhanced or natural bioprocesses for treating residual contaminant. The application of ISCO prior to biotreatment may offer an advantage to post-ISCO biotreatment by generating advantageous byproducts (Azadpour-Keeley et al., 2004; Droste et al., 2002, Sahl et al. 2007). For example, oxidants react with natural organic matter in the subsurface, generating dissolved organic carbon that can serve as a "food" source for microorganisms and enhance contaminant degradation (Sahl, 2005).

Byproducts generated during ISCO, however, can also challenge post-ISCO biotreatment. For example, metals potentially mobilized, along with pH changes, can affect microbial biotreatment, and these impacts are currently not well understood. Temporary perturbations in microbial activity post-ISCO that have been observed in some instances (e.g., Kastner et al., 2000, Klens et al., 2001, Bui and Cotton, 2002) are likely due to these changes in geochemistry. Field studies of coupled ISCO and