

Removal of arsenic from wastewaters and stabilization of arsenic bearing waste solids: Summary of experimental studies

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Abstract

One of the major research efforts at Montana College of Mineral Science and Technology has been the investigation of techniques for the treatment of arsenic bearing solutions and metallurgical solid waste materials. Experimental results from several Master of Science thesis studies are summarized in this presentation. Studies that are discussed include those that relate to: Arsenic removal from solution, stabilization of arsenic bearing waste materials, and recovery of arsenic from metallurgical waste and by-products.

1. Significance of the arsenic problem

The storage and disposal of waste residues containing arsenic, the disposal of arsenic-containing waste solutions, and the disposal of acid mine waters containing arsenic are common industrial problems. Many examples (of waste materials for which an acknowledged environmentally safe method of treatment and/or storage must be found) can be cited to illustrate the magnitude of the arsenic waste problem:

- Common sources of arsenic, industrial hydrometallurgical process problems, and the potential stability of arsenical residues were recently (1992) critically reviewed by Robins at an EPA Workshop on arsenic and mercury [1]. His conclusions included a summary of earlier research that demonstrated that a commonly used industrial process for removing arsenic from solution by precipitation as calcium arsenate produces a solid that is not stable in conventional chemical ponds (because carbon dioxide in air converts the calcium arsenate (and calcium arsenite) to calcium carbonate with the concurrent release of arsenic to the pond environment). Industry has now switched to ferric arsenate precipitation as the major means of removing arsenic from

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process waste solutions. However, Robins has also questioned the long term stability of this ferrihydrite precipitated ferric arsenate solid material. He has demonstrated that arsenic removal by ferric precipitation is via adsorption and not by the formation of ferric arsenate [2, 3]. Therefore, the long term stability of the ferric–arsenic product is presently unknown, questionable, and requires further study.

- Arsenic and arsenical compounds have been reported in waste streams from the metallurgical, glassware, wood preservation, ceramic, tannery, dye, and petroleum refining industries [4]. As well, the manufacturing of herbicides, pesticides, organic, and inorganic chemicals produces an appreciable quantity of arsenical waste [5, 6]. Examples include: over 5,000 tons/year of salt cake containing about one percent arsenic (K031 type waste) is produced by one company alone, i.e., the Fermenta Corporation at its Houston site [7]; over 14,000 tons of waste (K103) containing from 1–20 percent arsenic presently exists at the Whitmoyer Laboratories site in Pennsylvania [8].

- PEDCO assessed the potential release of arsenic from emerging energy technologies and concluded that over 4900 tons may be released per year by coal conversion processes alone (to evaporation ponds) [9].

- The treatment of large volumes of an arsenic bearing solution (300–400 mg/liter) at a large abandoned open pit mine is only now being considered (there is over 20 billion gallons of arsenic, copper, and zinc contaminated water) at Butte, Montana [10]. Treatment of this water is at least three to four years [11] in the future. The present proposed treatment technology (discussed later) may, indeed, be applicable to the treatment of this water.

- The entire Commencement Bay Nearshore/Tideflats region in northwestern Washington is presently being impacted by runoff water containing arsenic, copper, lead, and zinc that is leaching from logyards that used smelter slag as ballast and land fill material [12, 13]. The problem and technology of clean-up are presently under study.

- Groundwater contamination from TSD (Treatment, Storage, Disposal) facilities (both onsite and offsite) is a significant problem [14]. What makes the problem significant is not merely the number of sites or the quantity of wastes involved, but that the very concept of “disposal sites” has been changed by EPA regulations. Evolution of the “Banned Regulations” (the Land Disposal Restrictions for Certain “California List” (CL) Hazardous Wastes [15] requires that many substances considered safe in the past for disposal or storage now require treatment instead. The progression of such legislation (toward requiring treatment instead of mere storage or disposal) suggests the need for new technology or the need for more innovative use of known technologies.

The problem of safely disposing of arsenic bearing aqueous solutions is significant and has to date not been solved. Efforts at Montana College of Mineral Science and Technology are directed toward studies that may produce an acceptable solution to the arsenic solution disposal problem, i.e., the formation of stable arsenic bearing phases stable for long-term outdoor storage.

2. Studies at Montana College of Mineral Science and Technology

2.1. Arsenic removal from solution

Twidwell, Comba, Bowler, and Plessas [16–21] have been investigating the removal of arsenic from process and wastewater solutions by formation of filterable precipitates. The philosophy of the research is to form mineral-like precipitate solids that are stable in the natural environment.

Comba [17, 18] investigated the removal of arsenic from solution by the formation of mimetite, a lead chloroarsenate ($\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$). His results demonstrated techniques for successfully stripping aqueous arsenic concentrations from several grams per liter to below the detection limit for arsenic, i.e., the arsenic concentration was lowered to below 0.2 micrograms/liter (ppb), and has demonstrated the formation of phosphate/arsenate solid solution solids (phosphomimetite). The free energy of formation for mimetite was determined to be -625 ± 2 kilocalories/mole. The equilibrium stability diagram for the lead–arsenate–chloride system (using the determined free energy value) is presented in Fig. 1. The filterability of the mimetite was excellent because the morphology of the precipitate was small crystalline spherites. The lead left in solution could be stripped from solution as lead phosphate by the addition of phosphoric acid or by cationic ion exchange.

Because the lead chloroarsenate test work was so successful, attempts to form other chloro-, hydroxy- and phospho-arsenates (apatite like precipitates) have been made [17]. The preferred precipitant (for tailing pond storage) is lime. The presently used industrial process of ferric precipitation produces a solid that may [22–26] or may not be stable [2, 3, 27–29] for long term storage and the technique produces large volumes of waste that must be stored, i.e., the iron/arsenic mole ratio present during the precipitation must be greater than

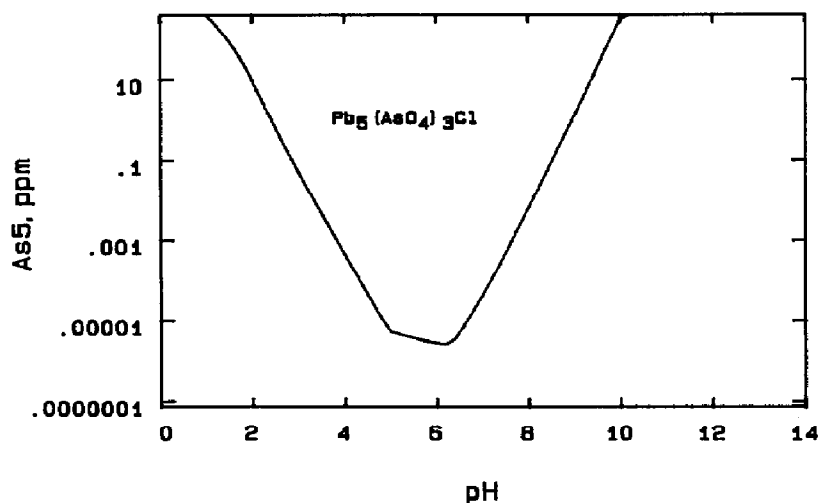


Fig. 1. Solubility of lead chloroarsenate as a function of solution pH. ($\text{Pb}^{2+} = 0.01$, $\text{As}^{5+} = 0.005$ and $\text{Cl}^- = 0.05$ M.)

four. Lime precipitation would produce less solids but stability must be assured. The data presented below illustrates the possibility of the required stability.

Lime (in increasing increments) was added to a series of bottles containing chloride, phosphate, and chloride plus phosphate solutions. Excellent arsenic removal was achieved and the results are presented in Table 1. These solution/solid mixtures have been aged in closed containers for approximately four years. Recent reanalysis of the solutions are also presented in Table 1. One sample from each test group, i.e., no additive, chloride additive, phosphate additive, and chloride plus phosphate additive, was chosen to determine the effect of pH on solubility. Each sample was split into two parts, the pH adjusted to either nine or ten, equilibrated for ten days, then analyzed for arsenic. The results are presented in Table 2. The solubility of arsenic in the calcium–arsenic system and in the calcium–arsenic–phosphorus–chloride system

TABLE 1

Arsenic removal from chloride and/or phosphate bearing solutions by lime additions

Sample	Moles added				pH	As (ppb)		
	As	P	Cl	CaO		Then ^a	Now ^b	New ^c
842	0.00062	0.0012	0	0.0088	12.65	0.5	0.64	6.4
845	0.00062	0.0012	0	0.0144	12.66	0.5	0.5	2.4
856	0.00062	0	0.0013	0.0075	12.61	<0.02	0.1	2.0
861	0.00062	0	0.0013	0.0161	12.62	<0.02	0.1	0.1
871	0.00062	0.0012	0.0038	0.0073	12.58	0.55		
872	0.00062	0.0012	0.0038	0.0088	12.59	0.5		
875	0.00062	0.0012	0.0038	0.0147	12.60	0.62	0.2	1.2

^aThen: Concentration two weeks after formation, 4 years ago.

^bNow: Same sample reanalyzed after 4 years storage.

^cNew: Concentration two weeks after formation, July 1992.

TABLE 2

Influence of solution pH on precipitate solubility

System (Sample No.)	Concentration (µg/l)		
	pH 9.0	pH 10.0	pH 12.6
Ca-As (828)	70,075	10,800	19.0
Ca-As-Cl (856)	19,160	5,975	0.1
Ca-As-P (845)	1,445	57.0	0.5
Ca-As-P-Cl (875)	1,386	45.0	0.2

are depicted in Fig. 2. Note that the arsenic solubility (in the chloride/phosphate bearing system), over the range of pH 9–12.6, is one to two orders of magnitude less than the solubility of calcium arsenate ($\text{Ca}_3(\text{AsO}_4)_2$).

Note (Table 2) that the phosphate bearing systems show essentially the same solubilities, i.e., the presence of chloride does not appear to be important. The solid phase (thoroughly washed) from the calcium–arsenic–phosphorus–chloride system was examined by SEM-EDX for elemental content. Chloride was not present. The same X-ray diffraction patterns were produced for the two systems.

The excellent stability of the phosphate/arsenate bearing solids (at pH levels present in tailings ponds) are presently being followed up as a part of an EPA supported study. The optimum conditions for the precipitation, i.e., the lime or calcite requirement, the phosphate concentration, and the mixing conditions; and the stability of the solid precipitate material to air (carbon dioxide) will be determined.

Bowler [20] investigated the removal of arsenic from solution by a variety of techniques. He accomplished essentially complete removal by precipitation/adsorption using calcium oxide additions. His results are in agreement with the results reported previously by Nishimura and Tozawa [30] and Robins and Huang [31]. The solid products pass the TCLP test for arsenic but, as has been reported by Robins [2], the solid product is not appropriate for long term chemical ponding storage.

Bowler [20] and Plessas [21] investigated arsenic removal by precipitation at elevated temperatures. They demonstrated that arsenic may be effectively removed from solutions by incorporation in the matrix of maghemite/magnetite.

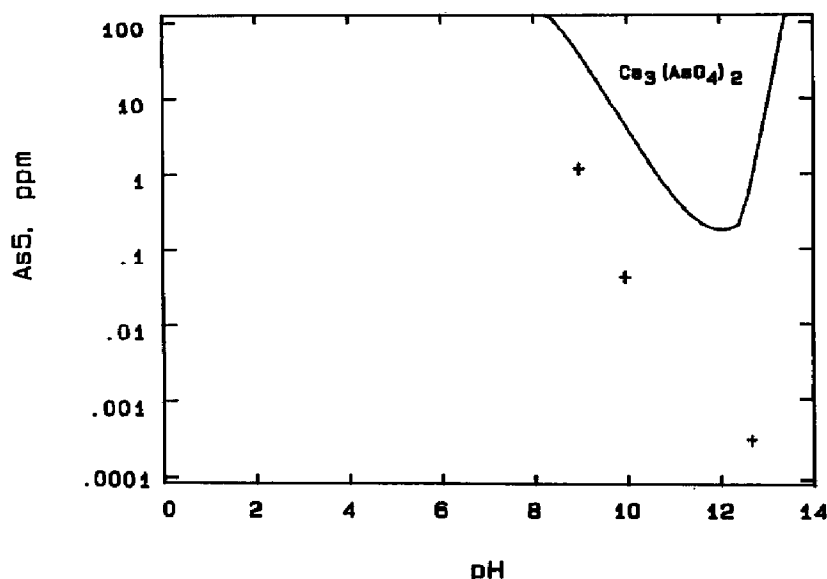


Fig. 2. Comparison between $\text{Ca}_3(\text{AsO}_4)_2$ solubility and solubility in the presence of phosphate. ($\text{Ca}^{2+} = 0.0147$ and $\text{As}^{5+} = 0.00062$ M; * means PO_4^{3-} present.)

The test work was conducted in the pH range 7–11 [20], 8–10 [21] at temperatures of 70–80 °C [20], 90 °C [21]. Successful arsenic removal was achieved to below the drinking water standard [20]. The precipitated products passed the TCLP test.

Honores [32] noted in a study (concerned with the recovery of metal values from copper smelter slags) that during the removal of copper by iron cementation more than 90% of the arsenic was also removed. Plessas [21] followed up on this noted effect and investigated arsenic removal by cementation using iron. She investigated the removal of arsenic from synthetic waste waters (at various pH levels) by flowing solutions over iron scrap (in a column setup). Arsenic concentrations less than the ICP detection limit (0.020 mg/l) were achieved at a pH level of 7. It is not presently clear whether the removal was by reduction of arsenate to arsenic metal or adsorption by oxidized iron on the surface of the iron scrap.

Plessas [21] also investigated the adsorption of arsenic by previously precipitated ferrihydrite (this removal technique differs from the work of coprecipitation reported by several investigators [22–25, 28–31]). The results showed that for effective arsenic removal rather large iron/arsenic mole ratios were required, see Table 3.

2.2. Stabilization of arsenic bearing waste materials

Four experimental studies have been conducted at Montana Tech on stabilization of solid waste materials. The technologies utilized were vitrification [33, 34] (one study) and cement/lime stabilization [8, 35, 36] (three studies). Twidwell and Mehta [33] proposed that a way to dispose of copper smelter flue dust was via conversion of the arsenic to calcium arsenate which could then be dissolved in copper smelter slag. Copper slags were doped with arsenic by dissolution of calcium arsenate in molten slag. Slags were then subjected to the EP toxicity test (Table 4) and also leach tested in a water environment for up to seven years. Arsenic release was minimal from the glassy slag test materials.

TABLE 3

Influence of ferric/arsenate mole ratio on arsenic adsorption from solution

Time (h)	Fe/As = 10 [As] (mg/l)	Fe/As = 14 [As] (mg/l)
0	1000	1000
0.5	411.7	<0.02
1	344.8	<0.02
2	294.9	<0.02
4	233.3	<0.02
8	137.2	<0.02
12	94.1	<0.02
25	34.6	<0.02

TABLE 4

EP Toxicity test results for doped copper reverberatory slags

As in slag (%)	Extraction solution analysis (mg/l)					
	As ^b	Cd ^b	Cr ^b	Pb ^b	Zn	Cu
0.5 ^a	0.016	0.093	0.016	0.226	0.30	0.239
0.8 ^a	0.047	0.000	0.007	0.149	0.010	0.474
2.1	0.448	0.000	0.006	0.169	0.082	0.526
3.3	0.421	0.000	0.004	0.150	0.084	0.270
5.2	0.901	0.000	0.007	0.150	0.151	0.294
9.1	0.415	0.001	0.007	0.148	0.060	0.050
19.4	0.802	0.002	0.007	0.149	0.036	0.008

^a As received (undoped) copper reverberatory slag.

^b EPA designated characteristic concentration for As, Cr, Pb is 5 mg/l; for Cd is 1 mg/l.

Three studies have been conducted that used cement or cement/lime mixtures for stabilizing various arsenic bearing materials, e.g., copper smelter flue dust [35], calcium and iron arsenate contaminated soils [8], and ferric hydroxide precipitated solids [36]. Tang [35] investigated the stabilization of copper smelter flue dust with cement/lime and the influence of stripping copper from flue dust (by a pyrometallurgical process) on the stability of the final arsenic bearing residue. He demonstrated as a part of his study that flue dust was stabilized by the addition of cement (25%) and lime (10%), i.e., the mixtures passed the TCLP test for arsenic, lead, and cadmium. This result was in agreement with test results generated by ARCO [37] (who have signed a ROD for disposal of 360,000 tons of flue dust by cement/lime stabilization). The findings of both studies agreed that passing the TCLP test required that sufficient cement/lime must be present to ensure that the TCLP solution pH be in the range 10–11.

A treatability study conducted by Twidwell and Chatwin [8] demonstrated that cement stabilization of calcium and iron arsenate/arsenite contaminated soils were not stabilized by cement alone. The presence of cement and a high pH in the TCLP test solution were not sufficient for the mixtures to pass the TCLP test. An additional stabilization roast [38] was required. A brief summary is presented in Table 5. The roast/cement stabilization technology was chosen as the alternative for clean-up.

A third study was conducted by Twidwell and McGrath [36] to evaluate whether organic arsenic (monosodium methylarsonate, MSMA) could be stripped from a salt brine solution (containing approximately two grams per liter arsenic) and the product stabilized by cement. Five solution treatment techniques were investigated (four precipitation and one solvent extraction). The final recommended procedure was ferric precipitation (with an iron/arsenic mole ratio of ten). The precipitation resulted in excellent removal, e.g., 2.3 g/l

TABLE 5

Stabilization of Whitmoyer NPL site materials

As content (%)	Cement/Waste	TCLP, mg/l (pH)
1.3	3	5.02 (11.3)
	3R ^a	0.11 (11.4)
	1	15.80 (11.0)
	1R ^a	0.43 (11.5)
	0.5	39.9 (11.6)
	0.5R ^a	0.45 (11.5)
17.8	3	5.0 (11.8)
	3R ^a	0.99 (11.7)
	1	72.2 (11.4)
	1R ^a	10.8 (10.3)

^aR designates roasting at 700 °C for one hour.

arsenic was reduced to 8–30 µg/l. TCLP results on the solid products ranged from 0.296 to 0.715 mg/l.

The products from the ferric stripping studies were subjected to roast stabilization (chosen because of the success achieved in the Chatwin, Twidwell study and the success achieved by Tozawa, Nishimura, and Umetsu [38]). Roast stabilization was unsuccessful. The roasted solids actually leached more arsenic in the TCLP tests than the unroasted precipitated products. Roasting in the presence of cement (1 part cement/1 part ferric product) was successful and resulted in TCLP values that were 3–5 times lower than the results on the untreated ferric product.

2.3. Recovering arsenic from metallurgical wastes and by-products

One of the major arsenic bearing metallurgical waste by-products from smelting is flue dust. Vast quantities of these flue dust presently exist; some containing up to twenty percent arsenic [11]. These flue dusts have and continue to be experimentally investigated at Montana Tech. Anderson [39] experimentally surveyed the use of a number of elevated temperature roasting techniques for recovering arsenic from copper smelter flue dusts. He specified optimum experimental conditions for removing arsenic as arsenic oxide from the dusts. Mehta [40] developed means for producing calcium arsenate (by roasting) in the flue dust and Mehta and Twidwell [34] investigated disposal of flue dust by dissolution in smelter slag. Their results demonstrated long term slag stability to water leach environments. Newhouse [41] and Arratia [42] applied the Copper Segregation Process [43] to the dust and to the dust mixed with lime, respectively. Arratia demonstrated that seventy percent of the copper could be recovered while retaining the arsenic in the solid residue.

Tang [35] studied the recovery of copper from cement/lime stabilized flue dust. He also demonstrated that 70% of the copper could be recovered. Neira [44] developed reductive roast processes of stripping arsenic from flue dust as relatively high purity metal. He recovered 99.5% arsenic metal as a product.

Several investigations have been performed to develop a process for producing copper without the formation of arsenic bearing flue dust. Beuerman and Twidwell [45, 46] investigated the recovery of copper from high arsenic concentrates (and the retention of arsenic in the concentrate residue) by a non-smelting segregation treatment. They demonstrated that more than 90% of the copper could be recovered from dead-roasted concentrates, but arsenic volatilization along with the copper was a problem. Gregory [47] continued the research to demonstrate complete retention of arsenic in the concentrate residue (without the emission of arsenic or sulfur dioxide gas) by a lime roasting/segregation process. He demonstrated over 90% copper recovery without any arsenic emission.

Other by-product treatment processes include studies by Flynn [48] to remove arsenic from lead blast furnace speiss as arsenic metal or as arsenic/antimony alloys; and by Peterson [49, 50] who developed techniques to recover arsenic and antimony from speiss as arsenic metal or as arsenic sulfide.

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