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Review

Treatment of metal finishing sludge for detoxification and metal value

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ABSTRACT

Metal-bearing hydroxide sludge wastes are generated by the metal finishing electroplating and electrochemical machining industries throughout the world. These wastes are classified as hazardous materials in the US and have traditionally been disposed of in hazardous landfill sites. Long-term maintenance of such sites is required, and metal values are lost unnecessarily. If metals are recovered from these sludge wastes, it will alleviate or reduce the disposal problem and provide for conservation of energy and metal resources. The treatment of hydroxide sludge materials for metal value recovery will produce several beneficial results, i.e. economic benefits from the metal values recovered will help offset the cost of recovery/treatment; nonrenewable resource metals will be recycled for use by society; and there will be significantly less hazardous material to be disposed of in landfills. Detoxification will have resulted because the metal content will have been removed to such an extent that the waste products successfully pass the USEPA toxic characterization test (TCLP), or, at least, the quantity of material that has to be disposed of in hazardous waste sites will have been drastically reduced.

The experimental results from several major USEPA studies and numerous master of science thesis studies are summarized in this presentation. A methodology to treat metal-bearing sludge materials by hydrometallurgical techniques is presented. The methodology emphasis is directed toward the application of known and industrially used hydrometallurgical technology, e.g., simple precipitation, solid/liquid separation, solvent extraction, and cementation unit operations. Electroplating and electrochemical sludge materials contain a unique mixture of metal species not normally encountered in natural ores and concentrates, e.g., iron, chromium, copper, zinc, cadmium, cobalt, and nickel. The demonstration that presently used industrial unit operations can be utilized for the treatment of these new materials is an important step forward in waste management and metal value recovery processing.

Keywords: Sludge; Electroplating; Electrochemical; Phosphate; Detoxification

1. INTRODUCTION

Most large-scale generators of electroplating or electrochemical machining sludge materials produce a multicomponent product. These sludge materials require that a multistage treatment sequence be used to economically recover the metal values. Most small-scale generators produce such a small quantity of waste material that they cannot afford to treat the material. Therefore, the most appropriate method of managing electroplating and electrochemical machining sludge from all sources is treatment in a centralized treatment facility. The USEPA has funded several major studies (Twidwell, 1984; Dahnke, 1986; Twidwell and Dahnke, 1988; Shuey and Twidwell, 2001) and several thesis studies (referenced later) directed toward the development of a process that would be appropriate for application in a centralized treatment facility.

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Waste Streams - The primary sources of hydroxide sludge material are the metal finishing, electroplating and the electrochemical machining industries. The treatment of rinse waters and the disposal of spent electroplating electrolytes by the metal finishing industry, as well as the treatment of contaminated electrolytes by the electrochemical machining industry, result in the production of these hydroxide sludge materials. The electroplating process (EP) creates large volume of rinse waters that contain relatively low concentrations of metal ions. These metal ions are removed from the rinse waters prior to disposal or recycle, by solution neutralization. The solution pH is raised to a level at which metal hydroxides precipitate from the solution. Spent electrolyte solutions are often disposed of by addition to the rinse water treatment system. The metal hydroxide solids produced by the precipitation process are separated from the solution by filtration. These solids are usually disposed of by transport to and placement in hazardous waste storage sites. The electrochemical machining (ECM) process is an electrochemical process that is used to produce intricate designs in superalloy materials. The machining is accomplished by controlled electrochemical dissolution of the part material. This dissolution requires an electrolyte with special properties, including a relatively high solution pH. The solution pH, usually approximately 8-9, is high enough that, as the part material is dissolved, the metals precipitate as metal hydroxide solids. The metal hydroxide solids are separated from the solution by filtration. These solids, especially if they are produced from superalloy material, contain high concentrations of nickel, chromium and sometimes cobalt, niobium, rhenium, and titanium. These solids are usually disposed of in hazardous waste sites, but because of their high value some are reprocessed.

2. PROCESS DESCRIPTION

Recovery of metal values from multicomponent metal hydroxide sludge materials has been effectively demonstrated by Twidwell, 1984; Dahnke, 1986; Twidwell and Dahnke, 1988; and Shuey and Twidwell, 2001. Conventional hydrometallurgical unit operations have been shown to be appropriate for selective recovery of copper, chromium, cadmium, cobalt, nickel and zinc. New technologies have been developed for the effective and economical separation of iron from chromium, i.e., via a phosphate precipitation process; and the separation of high purity cobalt from nickel by a cyanide precipitation process (both described later). The results presented in this presentation are based on sequential studies for a number of flowsheets, first on a bench scale and then on a small pilot scale. The overall study was conducted according to the following philosophy: investigations were conducted to ascertain whether known industrially used hydrometallurgical unit operations could be applied to complex multicomponent sludge leach solutions (Twidwell and Dahnke, 1988); evaluation of the phosphate precipitation process for simplifying the separation of iron and chromium from divalent cations (Dahnke, 1986); testing selected unit operations on a small pilot scale (Twidwell and Dahnke, 1988) and, developing an innovative technology for producing high purity cobalt and nickel (Shuey, 1992; Shuey and Twidwell, 2001). The detailed experimental procedures used to develop the treatment process are presented in each of the quoted studies. However, a typical study treatment sequence is described below:

- Each sludge was subjected to a standard optimized sulfuric acid leach, developed at Montana Tech (Twidwell and Dahnke, 1988), e.g., conditions for the standardized leach included: one-half hour residence time, 40-55°C, acid concentration of one gram acid per gram of solid in the sludge, an initial solid/liquid ratio of 0.8, and an agitation rate sufficient to suspend all particles in the solution phase. Residual solids were removed from the solution phase by vacuum filtration for the bench-scale tests and by a pilot-scale filter press for the large-scale tests.
- The leach solution was then treated for selective metal recovery. If the solution contained copper, it was removed by solvent extraction using LIX 622 at a nominal pH of 1.5-2; separatory funnels were used as the contactors for both loading and stripping solvent extraction experiments; counter-current flow, one-gallon mixer-settlers were used for the

pilot scale test work. The raffinate from the solvent extraction was then treated by mild oxidizing conditions to ensure that the iron was completely in the ferric form. Precipitation experiments were then performed on the mixed metal solution for iron and subsequently for chromium separation and removal.

- After the iron and chromium trivalent cations were removed, the solution was further treated for recovery of the divalent metals by various extraction techniques, such as cadmium removal by cementation, zinc recovery by solvent extraction, and nickel/cobalt recovery by precipitation as metal hydroxides.
- Nickel and cobalt were separated from each other by dissolution of the mixed metal hydroxides in a cyanide solution, strong oxidation to precipitate high purity nickelic hydroxide, precipitation of a cobaltous/cobaltic cyanide double salt, and subsequent recovery of the high purity cobalt by acid baking (to eliminate the cyanide and to produce a cobalt sulfate product).

The bench-scale test work was followed by small pilot scale tests (usually 200 pounds of sludge per test). The pilot scale test work was performed in 200 liter polypropylene reaction vessels equipped with heaters and agitators, one-gallon mixer-settler solvent extraction racks, and in a pilot-scale Ingersoll Rand filter press. The experimental conditions for the tests were based on the results of the optimized bench scale studies.

3. RESULTS AND DISCUSSION

A large database has been generated at Montana Tech for the treatment of a wide variety of sludge materials. Eleven master of science theses have been completed that are directly related to this project: Laney (1984) investigated the effectiveness of solvent extraction for removing copper from multicomponent sludge leach solutions; Dahnke (1986) summarized his research on zinc and iron recovery by solvent extraction, and his work produced the initial data upon which the phosphate process is based; Arthur (1987) investigated the application of the phosphate process to chloride-bearing sludge leach solutions; Konda (1988) investigated iron-zinc separations from high zinc solutions in a sulfate solvent matrix by selective precipitation of iron; McGrath (1988) studied the speciation of chromium in phosphate-bearing solutions and determined the kinetics of chromium phosphate precipitation; Rapkoch (1988) studied the recovery of iron and chromium by phosphate precipitation of their respective salts from an ammonia/ammonium system; Nordwick (1987) conducted studies on the effectiveness and the rate of conversion of ferric phosphate to ferric hydroxide; Quinn (1988) investigated the conversion of chromium phosphate to other more marketable products by soda ash fusion: Donelon (1989) investigated the application of the phosphate process to the treatment of stainless steel pickle liquors; Flynn (1990) investigated techniques to separate cobalt from nickel, and Shuey (1992) developed an innovative cyanide process for producing high purity nickel and cobalt from ECM sludge. These theses are presently available in published form from Montana Tech of the University of Montana, U.S.A. Because of the problem of summarizing such a large amount of data in the brief space available, the approach used in this presentation is to summarize the results and conclusions without including a great deal of detail. The authors are, therefore, relying on the reader to solicit copies of individual theses of interest.

Metal finishing sludge often contain a variety of potentially valuable elements, e.g., chromium, nickel, cobalt; less valuable elements but still of commercial importance, e.g., copper, zinc, cadmium; and impurity elements of no commercial value, but elements which must be removed because they would otherwise contaminate the recovered valuable product metals or salts, e.g., iron and calcium. The concentrations in which each element is present in EP and ECM sludge solids are extremely variable but the concentrations are often at levels high enough to provide commercial interest. Example sludge compositions are presented in Table 1.

Table 1
Example metal hydroxide sludge compositions

Element Composition in Solids, %									
Cu	Fe	Cr	Cd	Zn	Ni	Co	Al	Ca	Moisture, %
8.1	18.2	1.2	0.7	11.7	5.6	0.0	2.9	1.0	76.8
1.2	0.3	22.7	1.5	0.0	1.2	0.0	0.5	1,3	82.4
4.0	15.2	4.9	0.2	10.5	3.9	0.0	2.6	1.0	74.2
0.0	11.3	4.9	4.0	0.0	14.9	8.0	0.0	0.9	64.7
0.0	9.9	6.8	0.0	0.0	23.9	4.9	0.0	0.0	65.0

The discussion of results will be presented by following a typical sequence of unit operations applicable to a sludge material containing copper, iron, chromium, cadmium, zinc, cobalt, nickel, and calcium. The treatment of sludge waste containing these and other elements, e.g., titanium and niobium have also been investigated by Twidwell and Dahnke (1987, 1988). The unit operations to be discussed in this presentation include sludge dissolution by leaching; solid/liquid separation; solvent extraction of copper; precipitation of iron and chromium as phosphates, and their conversion to disposable or marketable products; cadmium recovery by cementation on zinc; zinc recovery by solvent extraction; cobalt/nickel recovery from the leach solution by precipitation with subsequent separation of the cobalt and nickel by cyanide processing. A typical flowsheet for the treatment sequence is presented in Figure 1 (Cu, Fe, Cr, Cd, Zn separation) and Figure 2 (Co/Ni separation). The unit operations are discussed below:

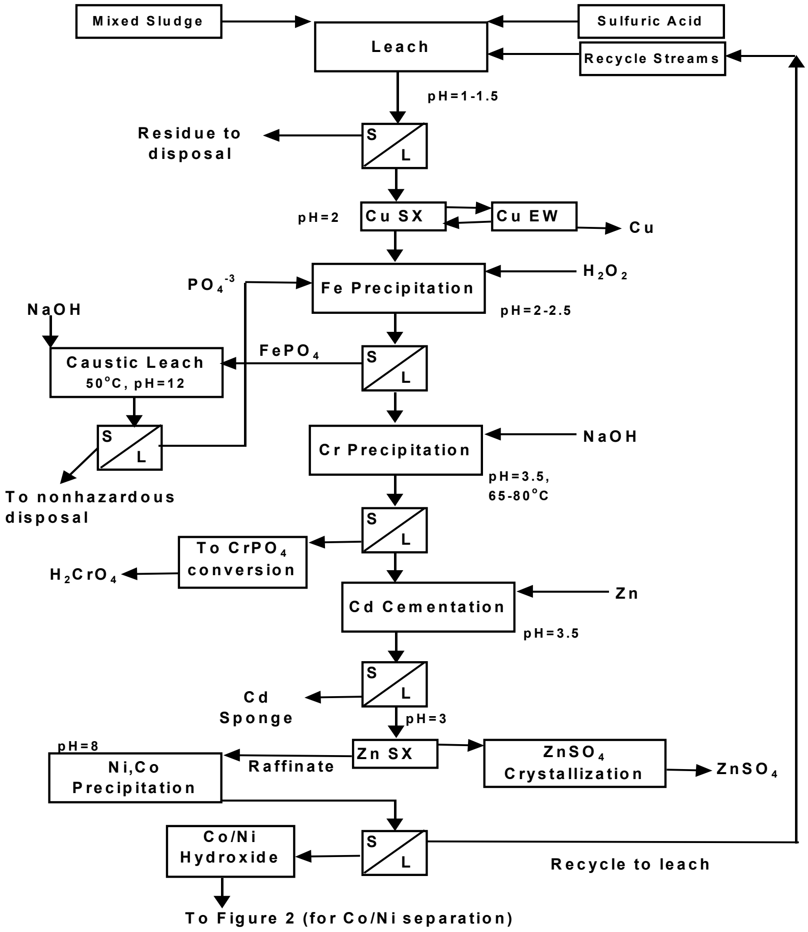

Figure 1. Flowsheet for the treatment of metal finishing sludge materials

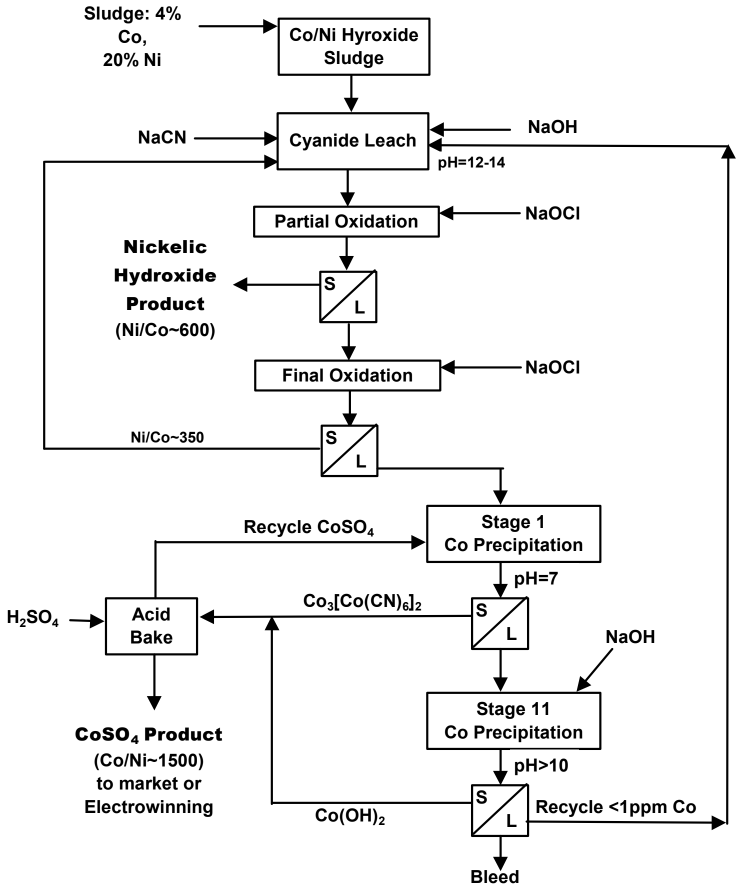

Figure 2. Flowsheet for the separation of high purity cobalt and nickel

3.1. Leach

Sulfuric acid leaching is effective and efficient in redissolving metal values (Twidwell, 1984; Dahnke, 1986; Twidwell and Dahnke,1987, 1988). The dissolution is rapid and without control problems. Conditions can be specified to achieve greater than 95% extraction of all metal constituents. Nominal conditions were described previously in the Process Description Section. Application of the standard leach procedure to a typical mixed metal sludge material produces a leach solution at a pH of approximately 1-1.5 and containing up to 80 grams per liter dissolved metals. Most of the sludge is redissolved, i.e., only about 10-15% of the initial sludge solids remain as a residue. Practically all the calcium present remains with the residue as calcium sulfate (the solution calcium concentration is less than 0.5 gram per liter). This residue may be considered hazardous, as is the starting electroplating sludge, and may have to be disposed of in the same manner as the starting sludge material but the quantity, of course, is greatly decreased. If titanium and niobium are present in the initial sludge they report to the leach residue and they may be recovered by subsequent residue processing. If copper is present, then the leach residue must be separated from the solution prior to copper extraction. If copper is not present, then the next unit operation would be the precipitation of ferric phosphate prior to the removal of solids. Precipitation of the ferric phosphate into the leach residue ensures that the combined leach residue/ferric phosphate solid mixture can be separated by a simple, effective solid/liquid separation because of the enhancement in the filtering properties provided by the presence of the ferric phosphate. Also, the leach residue-ferric phosphate mixture is considered nonhazardous according to the USEPA Toxicity Characteristic Leach Procedure (USEPA, 1986).

3.2. Solvent extraction of copper

Bench- and large-scale test work have shown that copper can be effectively and selectively removed from leach solutions containing appreciable concentrations of iron, chromium, zinc, cadmium, cobalt and nickel (Twidwell, 1984; Twidwell and Dahnke, 1988; Laney, 1984). Copper extractions greater than 95% from solutions (pH 1-1.5) containing about three grams per liter (g/l) copper, resulted in final raffinate solutions containing less than 30 milligrams per liter (mg/l, ppm) copper (using three stages of extraction, two stages of concentrated sulfuric acid stripping). Extraction of other metal ions from the leach solution by the organic reagent (LIX 622) was below analytical detection limits using Inductively Coupled Plasma (ICP) analysis. Degradation of the organic extractant does not appear to be important for the conditions tested. Deterioration of the organic extractant was not significant for solution conditions of high metal content, high ionic strength, the presence of phosphate, low pH, and mild (to 55°C) temperatures. The organic reagent was loaded and stripped for over 220 load/strip cycles. Non-degradation of the organic reagent (in a solution environment never tested before) is an important conclusion for not only long-term system operational stability but also for economics of the process.

3.3. Precipitation of ferric phosphate

Hydroxide sludge acid leach solutions contain a mixture of divalent and trivalent metal cation species. Ferric and chromium phosphate precipitation is an ideal way to selectively remove trivalent metal ions from divalent metal ions. The precipitation unit operation exhibits several important features:

- Selectivity for separating trivalent cations from divalent cations in an acidic solution is excellent.
- Solid/Liquid separation is excellent because of the precipitate morphology.
- Conversion of the phosphate precipitate to other more marketable products is possible.

Selectivity for removing trivalent cations from divalent cations can be predicted by use of solubility diagrams; an example for the separation of iron from nickel is presented in Figure 3 (Huang, 2001). Such diagrams have been used extensively during the development of the phosphate process.

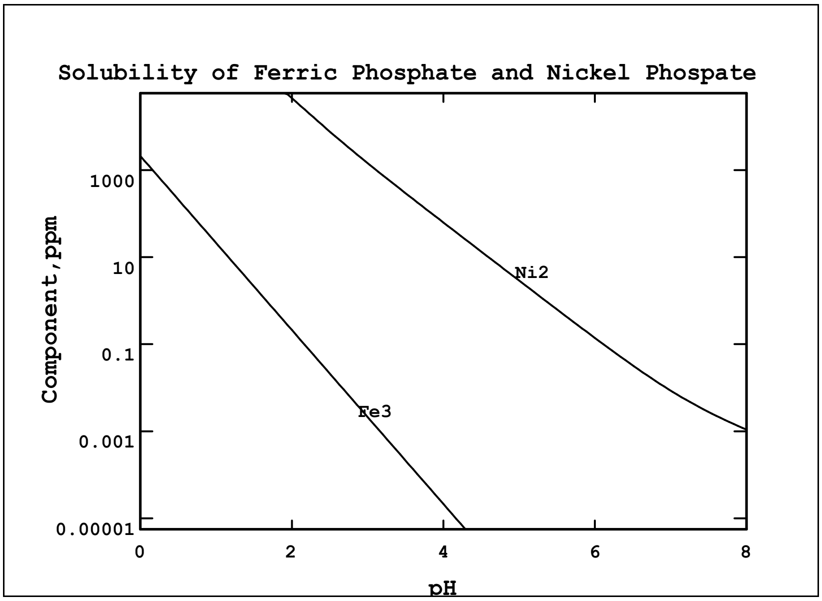

Figure 3. Relative solubility of ferric phosphate and nickel phosphate

In general, it can be stated that trivalent cation phosphates, under acidic conditions, are much less soluble than are divalent cation phosphates. Therefore, selective separations of trivalent cations from divalent cations are possible by controlling the solution pH. Effective solid/liquid separation is an important feature of the phosphate process. The morphology of the precipitated solids is small, dense, spherical particles. This is in contrast to hydroxide particulate that precipitate as high surface area solids. The phosphate particle morphology is therefore less amenable (than ferric hydroxide) to surface adsorption and contamination by other dissolved species. Also, an important feature of the phosphate process is that metal phosphates can be converted to more marketable products with the regeneration of phosphate reagent for recycle. Iron phosphate can be converted to ferric hydroxide for disposal by a simple elevated caustic leach (Nordwich, 1987). Bench-scale test work showed and large-scale test work confirmed that phosphate precipitation is an effective and very selective way of removing iron from an acidic mixed metal solution (Figures 4 and 5) (Twidwell and Dahnke, 1988; Arthur, 1987; Donelon, 1988). Important features of the precipitation process include:

- Precipitated particle morphology is spherites and agglomerates of spherites (Figure 6). Because of the morphology, the filterability of the precipitated ferric phosphate is excellent, i.e.; the filterability is about one hundred times better than that of precipitated ferric hydroxide.
- Precipitation is rapid and is essentially complete at room temperature in a residence time of 0.5-1.0 hour. Precipitation to less than 20mg/l (ppm) can be accomplished from a room temperature solution at a pH of 2.5 without chromium, nickel, zinc, or cadmium coprecipitating (Figures 3, 4 and 5). In fact, iron can be selectively stripped from a solution containing 30 grams per liter iron and 150 grams per liter zinc without appreciable zinc contamination, i.e., <1% zinc in the final solid product (Konda, 1986).
- Ferric phosphate precipitation-pH curves are essentially the same regardless of the media and aqueous metal species present, i.e., sulfate (Twidwell and Dahnke, 1988; Konda, 1986), chloride (Arthur, 1987), nitrate (Arthur, 1987), or ammonium (Rapkoch, 1988) solutions.
- Ferric phosphate can be converted to ferric hydroxide with the regeneration of phosphate reagent for recycle by leaching in a caustic solution at a pH of 12 at 50°C (Nordwick, 1987). The precipitated ferric phosphate and the converted ferric hydroxide product both pass the TCLP test and, therefore, can be disposed of as nonhazardous solids (Twidwell and Dahnke, 1988).

3.4. Precipitation of chromium phosphate

Bench-and large-scale pilot test work showed that chromium could be very effectively stripped selectively from divalent cations by phosphate precipitation. Important features of the precipitation process include:

- Precipitated particle morphology is spherites and agglomerates of spherites. Therefore, filterability is excellent (Figure 7).
- Chromium phosphate precipitation is very temperature-time dependent. Ambient temperature precipitation does not begin until the solution pH is raised to at least 3.3, but precipitation is essentially complete at a pH of 3 at 80°C (Figure 8). The influence of time and temperature on the precipitation solubility curve is very important because it allows for good iron-chromium separations based on the relative rate of precipitation of the ferric phosphate at ambient temperature compared to the rate of precipitation of the chromium phosphate (McGrath, 1988).
- Selective separation of chromium from nickel is excellent, even up to temperatures of 80°C (Figure 9).
- Chromium phosphate has a limited marketability. It has been demonstrated that it can be effectively converted to more marketable feedstocks, such as sodium chromate or chromic acid, by a soda ash fusion process (Quinn, 1988). The fusion process converts the chromium phosphate to sodium chromate. The sodium chromate is water-soluble and a simple leach results in a relatively high purity sodium chromate solution. This product can be marketed or further processed to chromic acid.

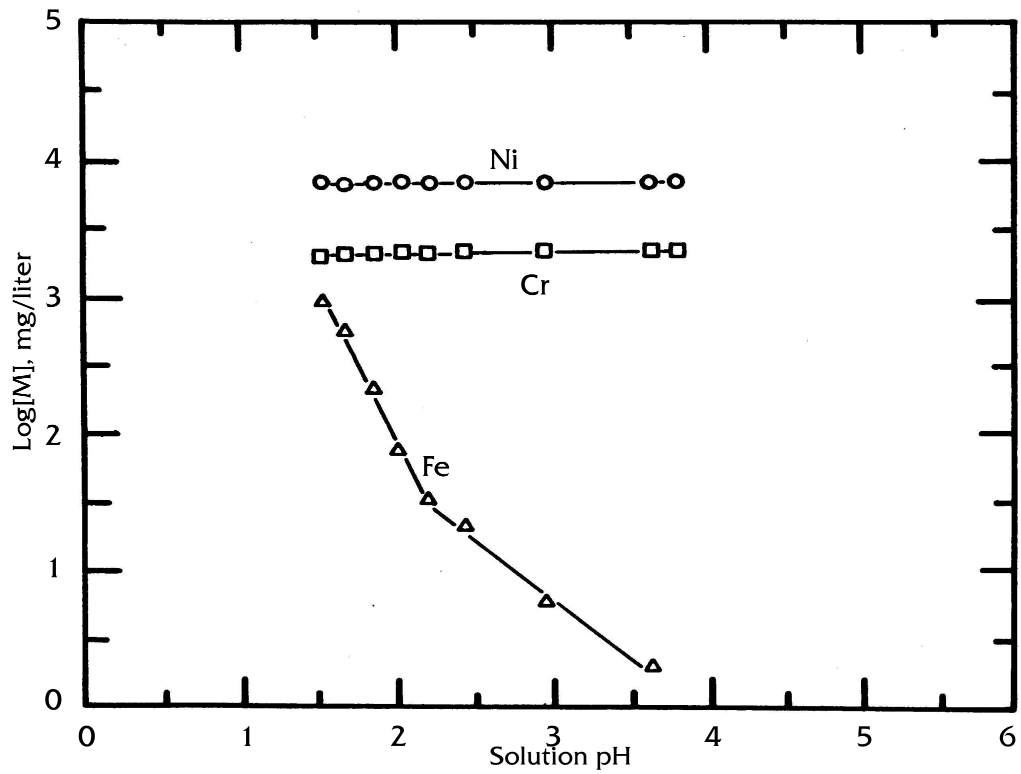

Figure 4. Selective removal of iron from chromium and nickel in mixed metal hydroxide leach solutions

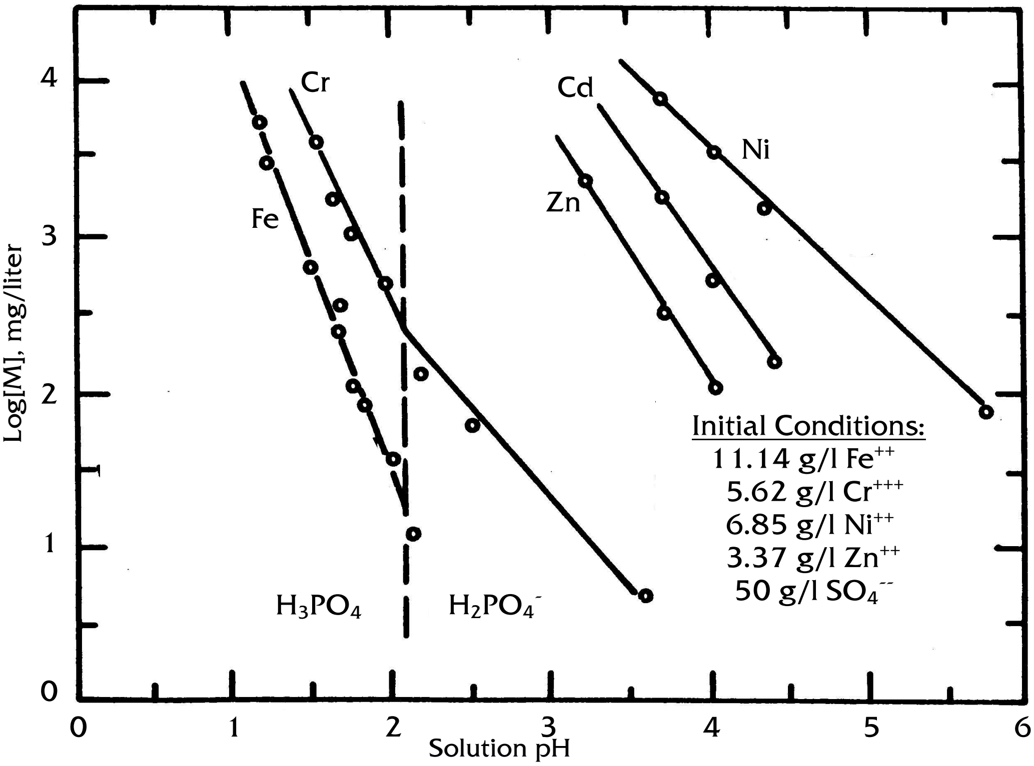

Figure 5. Selective precipitation of chromium and iron from divalent cations in mixed metal hydroxide leach solutions

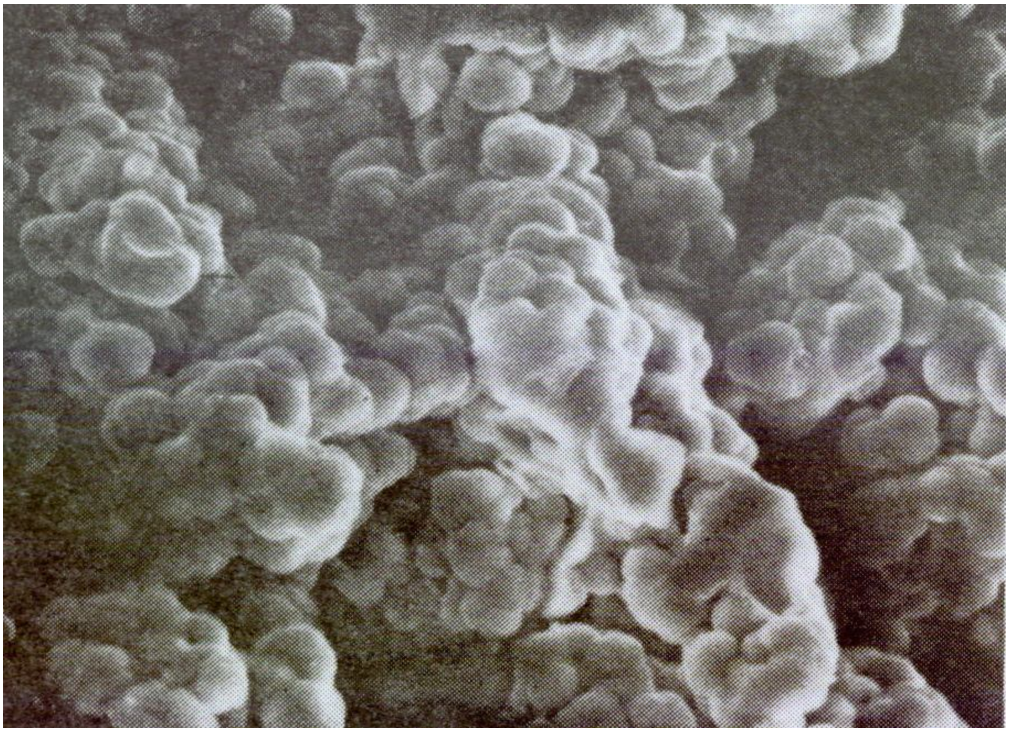

Figure 6. Photomicrograph of ferric phosphate particles precipitated from a mixed metal hydroxide leach solution (50x)

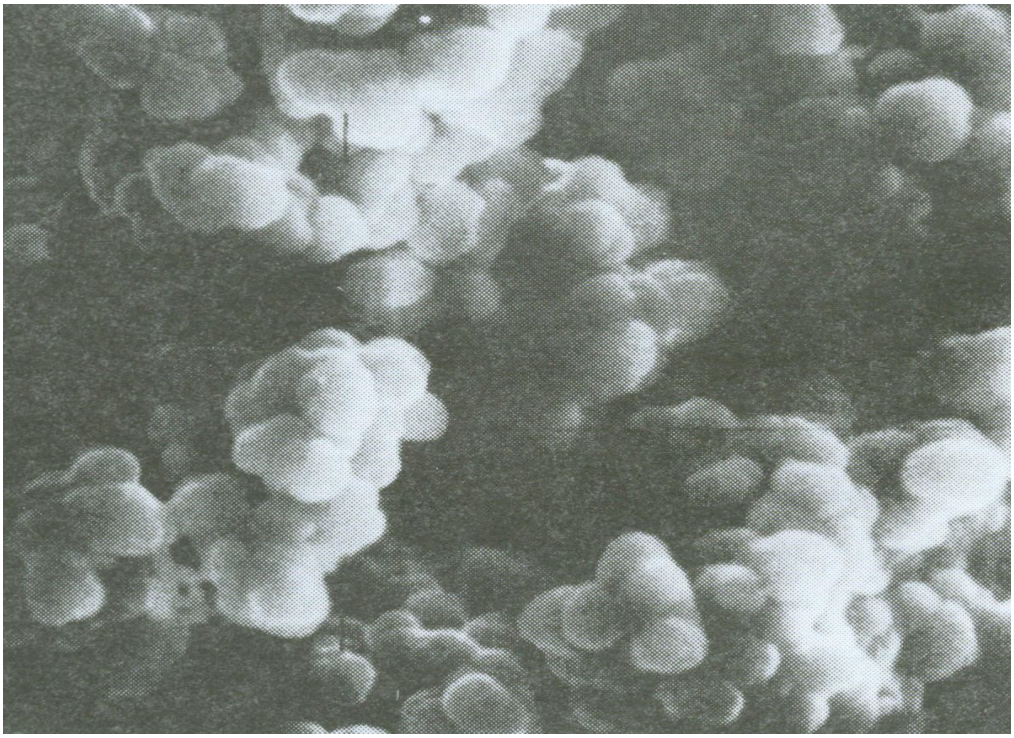

Figure 7. Photomicrograph of chromium phosphate particles precipitated from a mixed metal hydroxide leach solution (50x)

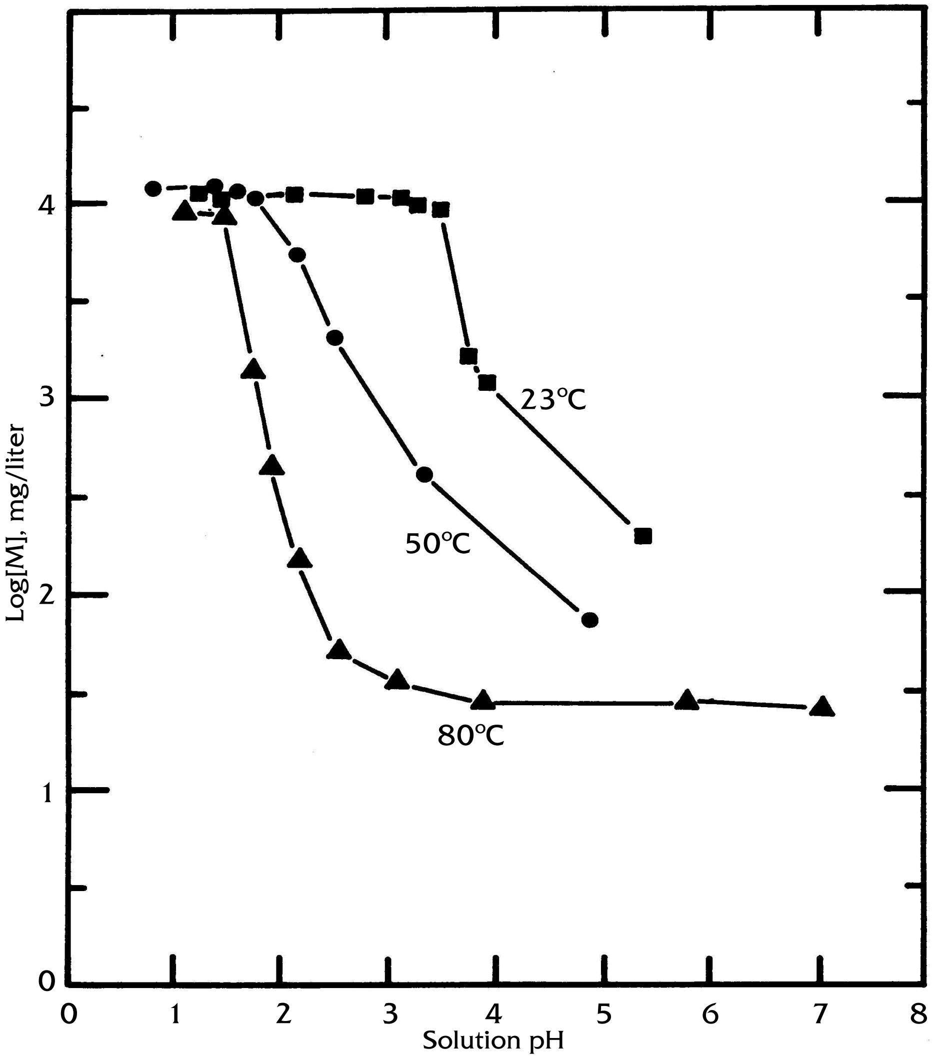

Figure 8. A comparison of solubility curves for pH scan tests on chromium solutions at 25°C, 50°C, and 80°C

3.5. Cadmium cementation

Cadmium can be selectively separated from the solution by cementation on zinc. This is a widely practiced industrial unit operation (Normua, 1983). The cementating reagent is zinc. Cadmium is precipitated onto the zinc surfaces, and the product is recovered from solution by filtration. This is an electrochemical exchange process, and zinc ions enter the solution as the cadmium plates out. The zinc that enters the solution phase and the zinc present as a result of the original leach can be subsequently recovered by solvent extraction. The product from this unit operation is sponge cadmium, e.g., 80-85% Cd.

3.6. Solvent extraction of zinc

At this point in the sequential treatment sequence only zinc, nickel and cobalt remain in solution. Pilot scale test work (one gallon mixer/settlers) has demonstrated that zinc can be very effectively continuously extracted from solution by solvent extraction using di-ethyl hexyl phosphoric acid (DEHPA) as the extractant and subsequently stripped by 150g/L sulfuric acid (Twidwell and Dahnke, 1988). Zinc extractions of better than 98% from solutions containing up to approximately twelve grams per liter zinc were achieved without contamination by nickel or cobalt. Three stages of solvent loading and two stages of solvent stripping were utilized. Deterioration of the organic solvent extraction reagent for extended load/strip cycling was shown not to be a problem. However, any calcium present in the leach solution will also be extracted by the DEHPA extractant. The calcium is stripped from the DEHPA concurrently with the zinc by the strip acid (sulfuric acid). However, the calcium precipitates from the strip solution as crystalline calcium sulfate solid. This solid can be readily removed from the strip circuit by filtration.

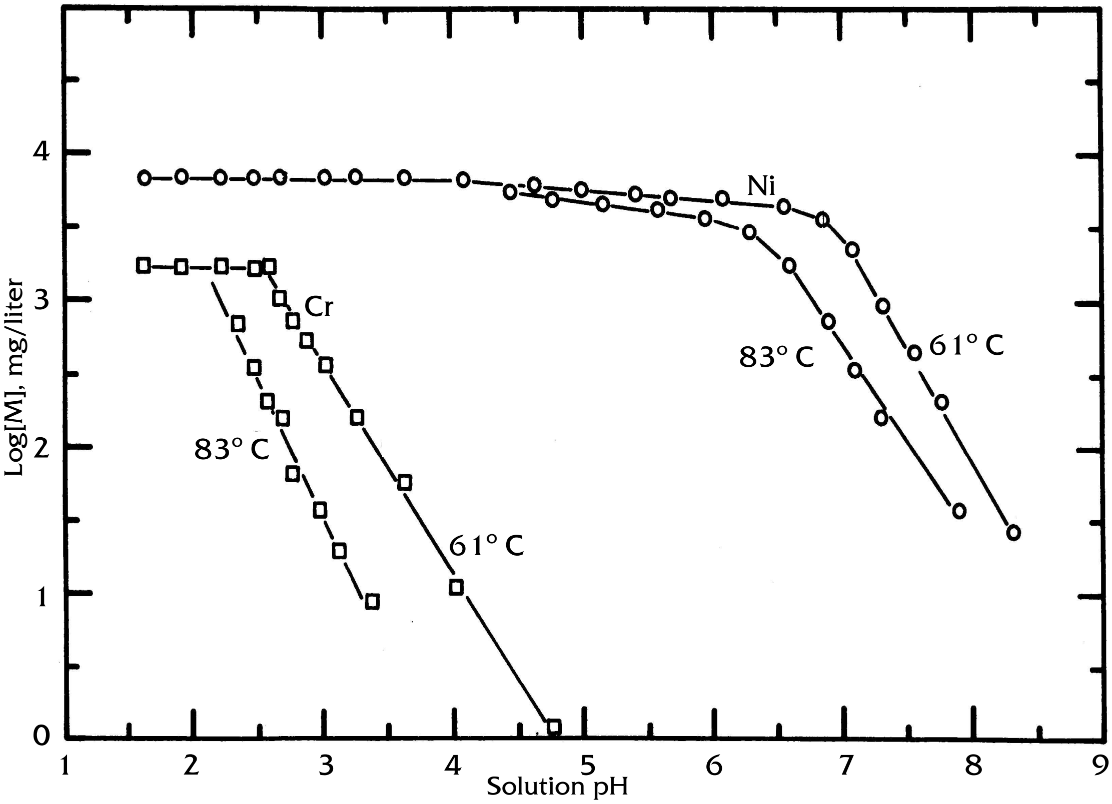

Figure 9. A comparison of solubility curves for pH scan tests on chromium and nickel solutions at 61°C and 83°C

3.7. Precipitation of nickel/cobalt

Nickel can be stripped from the leach solution by precipitation as nickel phosphate, nickel hydroxide, nickel sulfide, or nickel carbonate, or it may be recovered from solution by solvent extraction and electrowinning. Sludge materials containing the above discussed elements and nickel (no cobalt) have been subjected to pilot scale processing. Large-scale test work at Montana Tech has been directed toward nickel recovery by sulfide precipitation. Nickel removal to below six ppm was achieved.

If nickel and cobalt are present in the leach solution then the treatment route is to precipitate nickel and cobalt hydroxide by pH control. Shuey (1992) and Shuey and Twidwell (2001) have demonstrated an innovative technology for selectively separating nickel and cobalt into relatively high purity products, e.g., nickel hydroxide (Ni/Co weight ratio of 600/1 in the product); cobalt sulfate (Co/Ni weight ratio of 1500/1 in the product). This technology (Figure 2) consists of leaching the mixed hydroxide solids in a cyanide solution. Nickel and cobalt cyanide aqueous complexes form (pH≅12). The solution is then oxidized with hydrogen peroxide or hypochlorite. The nickel cyanide aqueous complex is destroyed and nickelic hydroxide precipitates and is removed from the solution. The cobalt cyanide solution is then treated by adding cobaltous (cobalt sulfate) to the solution. A cobaltous cobaltic cyanide double salt solid forms and is removed from solution. The double salt is then subjected to a sulfuric acid bake to destroy the cyanide and to form high purity cobalt sulfate. Part of the cobalt sulfate product can be marketed and part can be recycled to the process circuit as the reagent for the formation of the double salt.

4. CONCLUSIONS

Bench-scale tests have shown and large-scale tests have confirmed that metal finishing sludge materials can be effectively treated for metal value recovery. The products that result are of sufficient purity to serve as feedstock for commercial uses, or they can be used for conversion to other, more marketable products. The proposed treatment process consists of known hydrometallurgical unit operations, and simple, readily available equipment can be utilized, i.e., simple stirred reactors, solvent extraction system vessels, thickeners, and solid/liquid separation devices. Economic estimates have been presented by Twidwell and Dahnke (1984, 1987, 1988) and by Shuey and Twidwell (2001) that suggest that the treatment of metal hydroxide sludge materials could be accomplished on a scale of 30-50 tons/day at a substantial profit. Also, metal finishing sludge materials are classified as hazardous waste and their disposal as such results in appreciable loss of metal values. Society would benefit from processing these materials because nonrenewable metals will be recovered and disposal of the materials as hazardous wastes will not need to be practiced.

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