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A GUIDE to FIFTY YEARS of RESEARCH at MONTANA TECH: Part 2 THE TREATMENT of ELECTROPLATING and ELECTROMACHINING METAL HYDROXIDE SLUDGE for the RECOVERY of METAL VALUES [see also Part 1)

Larry G. Twidwell

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A GUIDE to FIFTY YEARS of RESEARCH at MONTANA TECH: Part 1 THE TREATMENT of ARSENIC, SELENIUM, THALLIUM, METAL BEARING SOLUTIONS and WASTE SOLIDS [Available at Research Gate **www.researchgate.net/profile/Larry_Twidwell/contributions/?ev=prf_act.**
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ABSTRACT and FORWARD

The treatment and recovery of metal species from hydrometallurgical solutions and wastewater solids has been and continues to be an important research topic. This presentation includes a guide to the literature with a summary discussion of the research conducted at Montana Tech in the Department of Metallurgical and Materials Engineering during the 1984-2001 period. A previous presentation (Part 1) focused on the removal of arsenic, selenium, and other species by hydrometallurgical processes and the formation of environmentally stable disposable products. This guide is available at the reference presented above.

This following presentation (Part 2) is based on the research of Master of Science graduate students (13), industrial (3) and academic colleagues (4), at the Montana College of Mineral Science and Technology (which morphed to Montana Tech [1977], then to Montana Tech of The University of Montana [2000], then to Montana Technological University [2019). The referenced research of each of the graduate students (13) in this presentation is gratefully acknowledged. The following summary does not include other research studies conducted in the Metallurgy/Materials Engineering Department by other teaching and research colleagues. See Appendix C for a list of the Master of Science research thesis students and their research topics highlighting their contributions to our departments' research efforts (student theses are readily available, on-line in digital format, at the Montana Tech Library).

The referenced research discussed (and annotated) in this report was supported by the U.S. Environmental Protection Agency (EPA) over a period of ten years.

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THIS PRESENTATION

Twidwell and Dahnke published the results of a ten-year study to establish a treatment for detoxification and metal value recovery from metal finishing (electroplating and electromachining) sludge. The reference quoted below is presented here with additional supplementary information appended ***(Twidwell and Dahnke, 2001, Treatment of Metal Finishing Sludge for Detoxification and Metal Value Recovery, European Journal of Mineral Processing and Environmental Protection (EJMPEP), Vol 1, No 2, pp 76-88***).

Please note: As a convenience to readers using this presentation as a guide to the subject literature, all references are bolded and highlighted throughout the text.

INTRODUCTION

"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." **(Twidwell and Dahnke, 2001), A Review: *Treatment of Metal Finishing Sludge for Detoxification and Metal Value Recovery, EJMPEP, Vol 1, No 2, pp 76-88).***

BACKGROUND

Electroplating/Electromachining

"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 **(Twidwell and Dahnke, 2001).**

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 and thirteen **Master of Science** thesis studies **(Twidwell and Archibald, 1983; Twidwell, 1983, 84; Dahnke, 1985; Twidwell and Dahnke, 1986, 1987, 1988, 2001; Shuey, 1992; Shuey and Twidwell, 2001)** directed toward the development of a process that would be appropriate for application in a centralized treatment facility.

Treated 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" **(Twidwell and Dahnke, 2001).**

PROCESS DESCRIPTION

Recovery of metal values from multicomponent metal hydroxide sludge materials has been effectively demonstrated by **Twidwell, 1984; Dahnke, 1986; Twidwell and Dahnke, 1988a, 1988b, 2001; 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, 1988a)**; evaluation of the phosphate precipitation process for simplifying the separation of iron and chromium from divalent cations **(Dahnke, 1985)**; testing selected unit operations on a small pilot scale **(Twidwell and Dahnke, 1988a)** and, developing an innovative technology for producing high purity cobalt and nickel **(Shuey, 1992; Flynn, 1990 ; 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, 1988a),** 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).

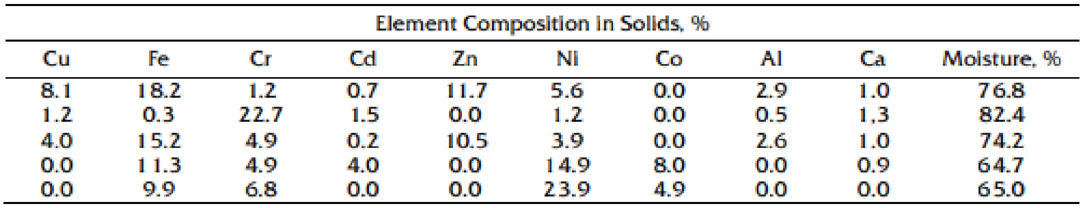
The bench-scale test work was followed by small pilot scale tests (usually 200 pounds of sludge per test). The pilot scale test work was performed in 200-liter polypropylene reaction vessels equipped with heaters and agitators, one-gallon mixer-settler solvent extraction racks, and in a pilot-scale Ingersoll Rand filter press. The experimental conditions for the tests were based on the results of the optimized bench scale studies" **(Twidwell and Dahnke, 2001).**

RESULTS AND DISCUSSION

A large database has been generated at Montana Tech for the treatment of a wide variety of sludge materials. Thirteen 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 (1985)** 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; **Downey (1986)** investigated the use of solvent extraction to recover chromium and nickel; **Konda (1986)** investigated iron zinc separations from high zinc solutions in a sulfate solvent matrix by selective precipitation of iron; **Arthur (1987)** investigated the application of the phosphate process to chloride-bearing sludge leach solutions; **Rapkoch (1987)** 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**.** **McGrath (1992)** studied the speciation of chromium in phosphate-bearing solutions and determined the kinetics of chromium phosphate precipitation; **Donelon (1989)** and **Leary (1990)** 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 is presented 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, 1988a, b, 2001).** 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).

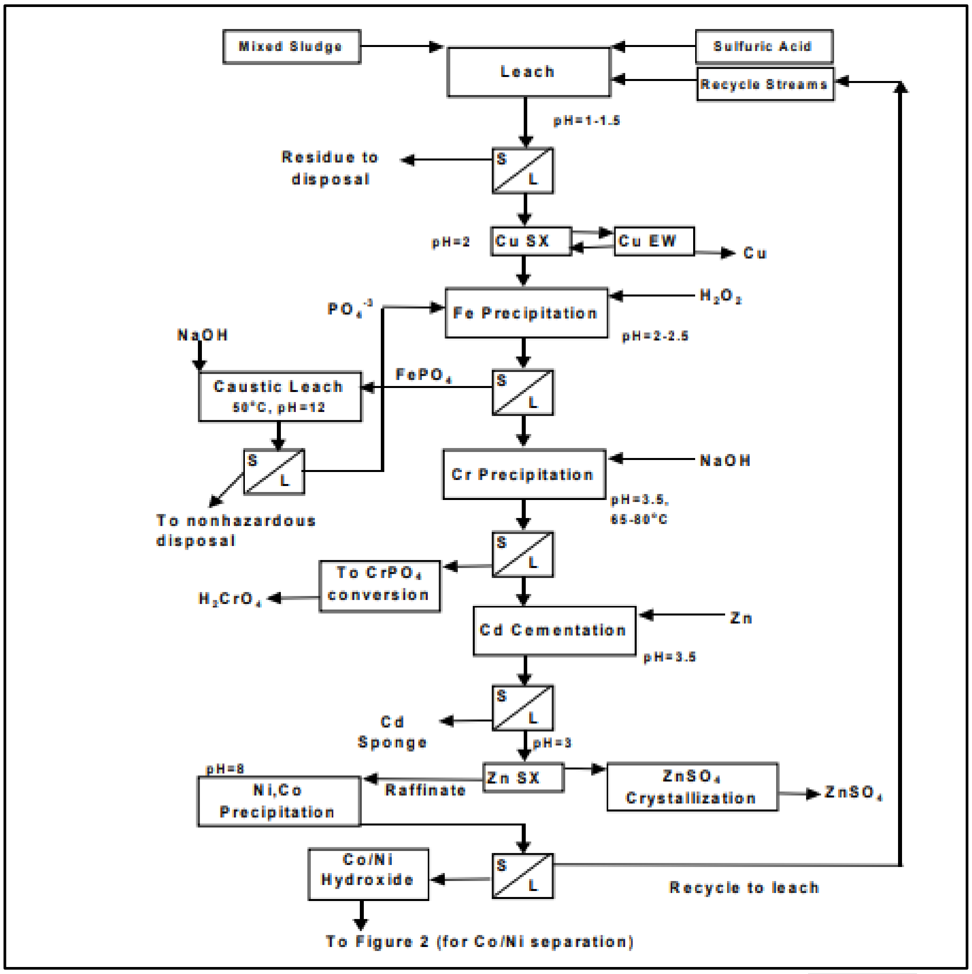


Figure 1. Flowsheet for the treatment of metal finishing sludge materials (Twidwell and Dahnke, 1987, 2001)

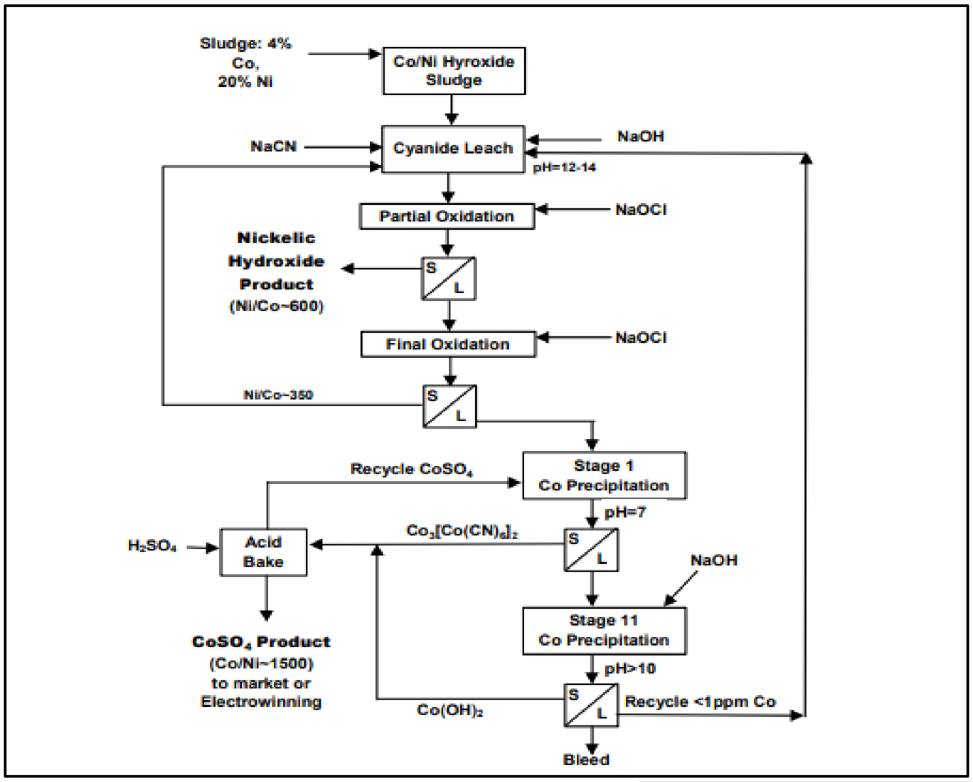


Figure 2. Flowsheet for the separation of high purity nickel and cobalt (Twidwell and Dahnke, 1987, 2001)

The unit operations for each treatment unit operation are discussed below:

Treatment Sequence One (Figure 1)

1. **Leach**

Sulfuric acid leaching is effective and efficient in redissolving metal values **(Twidwell, 1984; Dahnke, 1986; Twidwell and Dahnke, 1987, 1988, 2001).** 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 (TCLP) **[USEPA, 1986].**

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; Downey, 1982; 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. 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 were used extensively during the development of the phosphate process.

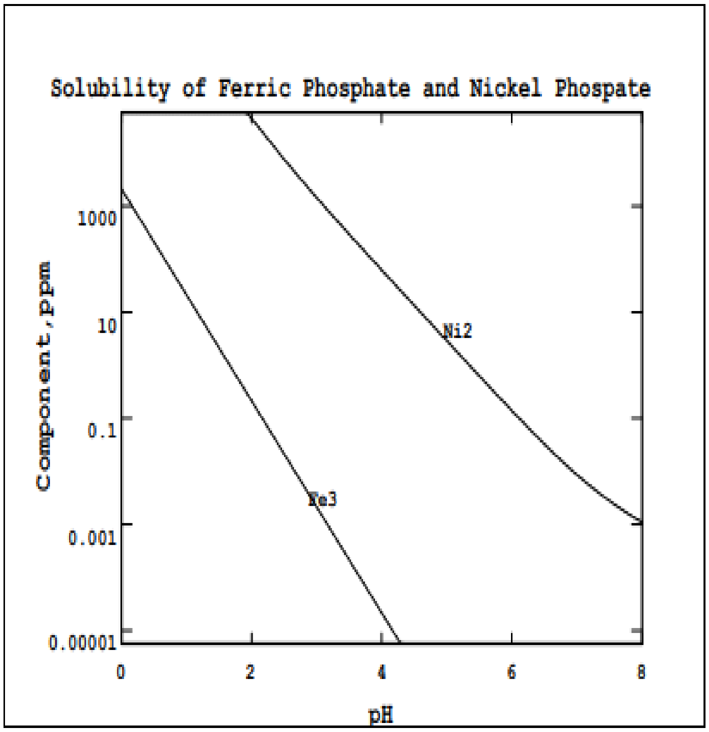


Figure 3. Relative solubility of ferric phosphate and nickel phosphate

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).** Key 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 20 mg/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, 1987)** 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).**

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, 1992).**
- 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.

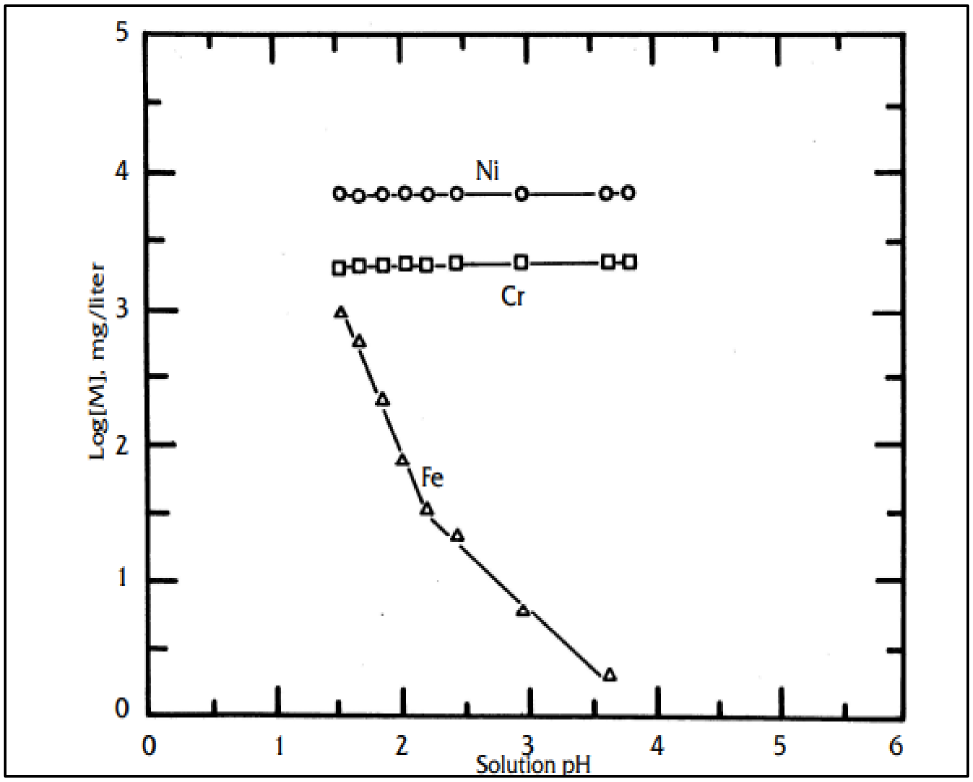


Figure 4. Selective removal of iron from chromium and nickel in mixed metal hydroxide leach solutions

(Note: ferric iron can be removed from chromium and divalent elements at ambient temperature, i.e., trivalent chromium precipitation does not occur at ambient solution temperature; so ferric can be removed first at ambient temperature then chromium can be removed in preference to the divalent cations by treating the solution at >50°C).

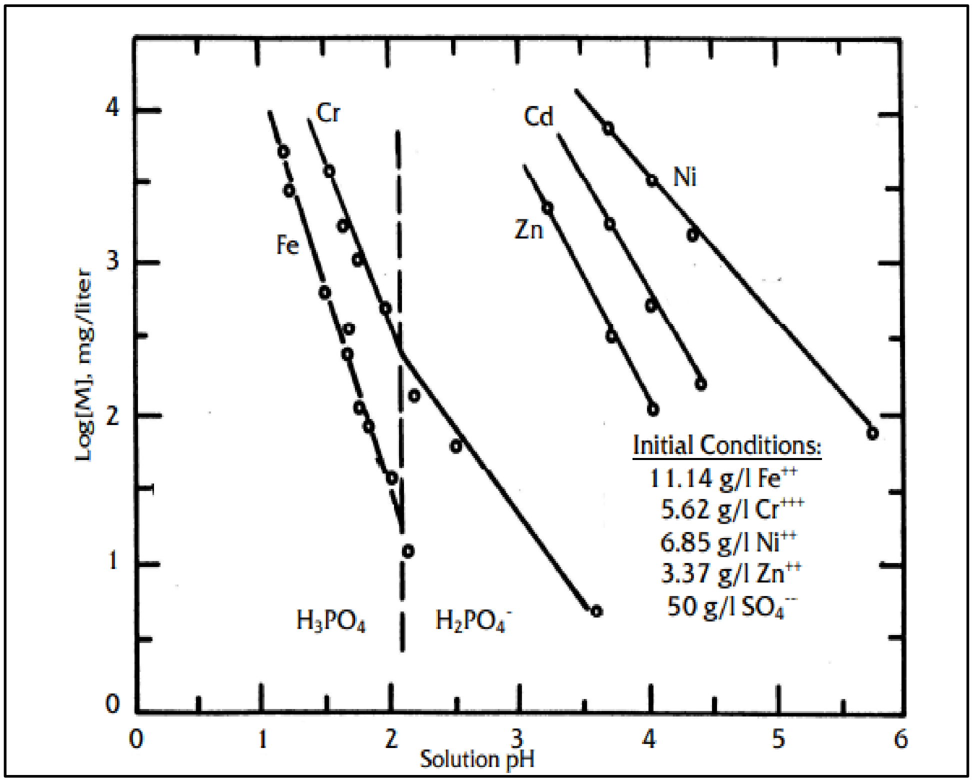


Figure 5. Selective removal of chromium and iron from divalent cations in mixed metal hydroxide leach solutions at an elevated temperature of >50°C

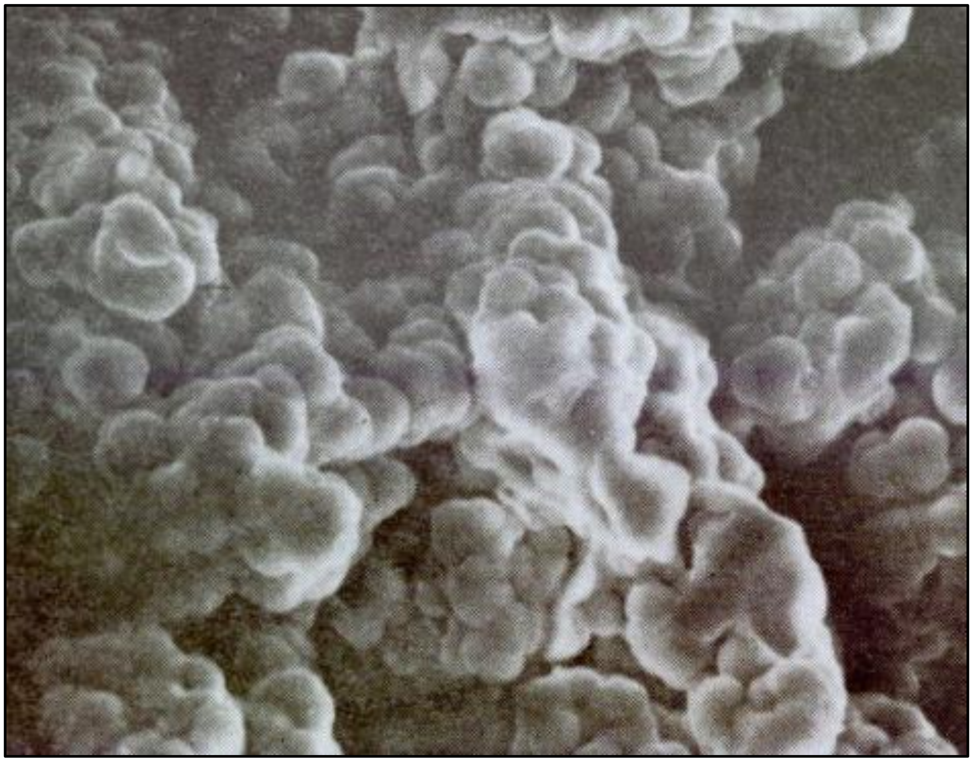


Figure 6. Photomicrograph of ferric phosphate particles precipitated from a mixed metal hydroxide. leach solution (50x)

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

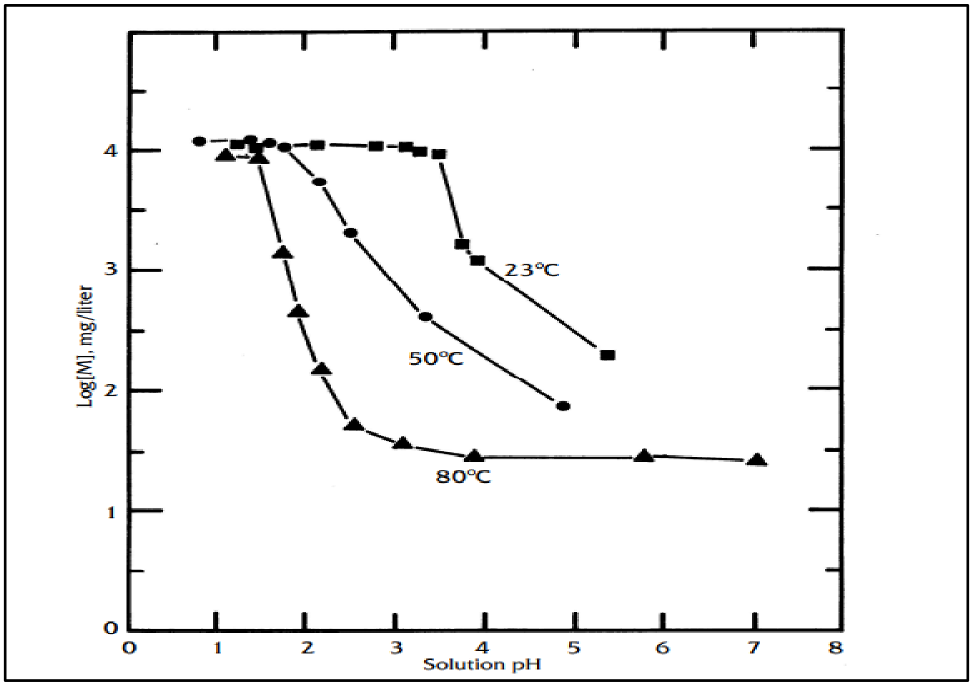


Figure 8. A comparison of solubility curves for pH scan tests on chromium solutions at 25°C, 50°C, and 80°C

5.0 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 cementation 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.

6.0 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 hexyphosphoric 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

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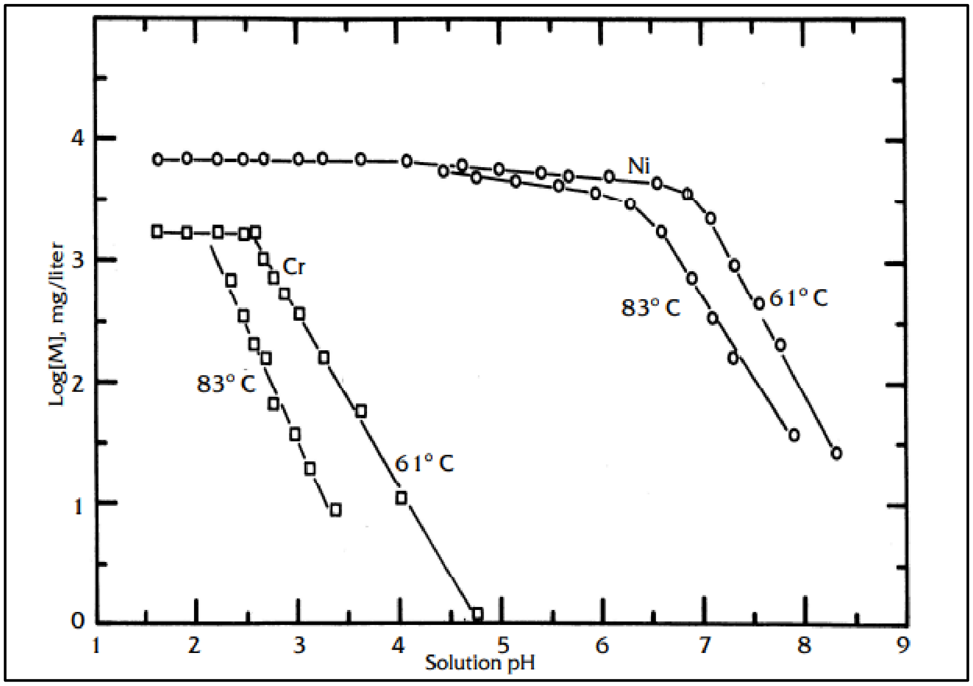

Figure 9. A comparison of solubility curves for pH scan tests on chromium/nickel solutions at 61°C and 83°C

7.0 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 mg/L was achieved.

Treatment Sequence Two (Figure 2)

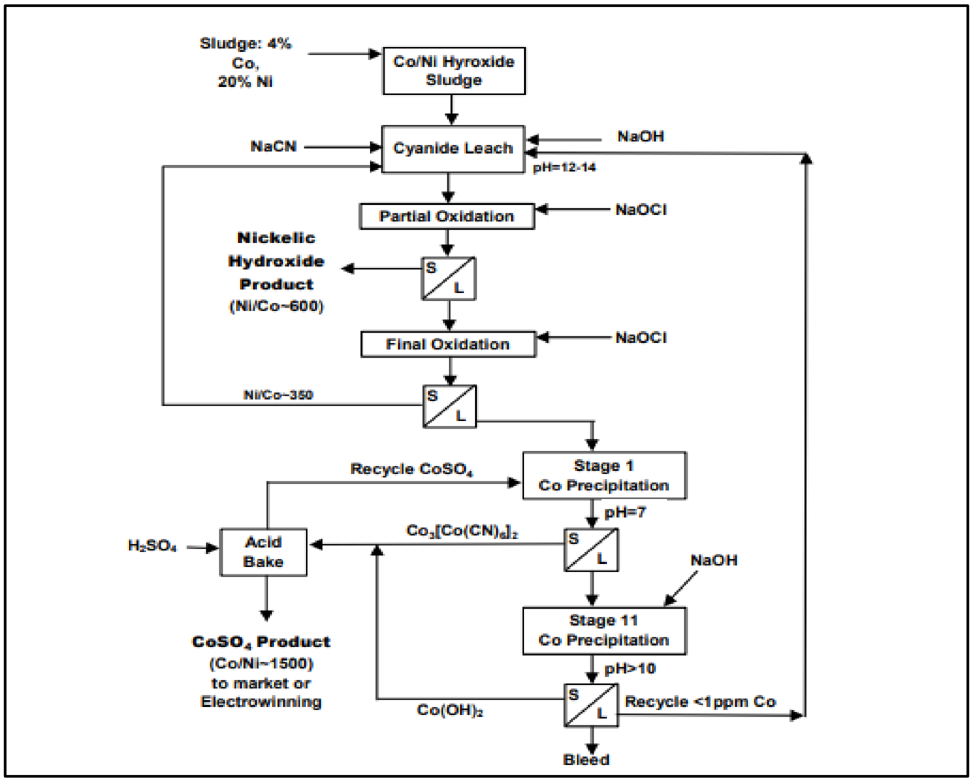

Figure 2. Flowsheet for the separation of high purity nickel and cobalt (Figure repeated as a convenience to the reader)

Separation of High Purity Nickel and Cobalt

If nickel and cobalt are present in the leach solution, then the treatment route is to precipitate nickel and cobalt hydroxide by pH control (as described above for Sequence One). **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 an elevated pH 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 (in preference to cobaltic cyanide) 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. 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.

CONCLUSIONS

Bench-scale tests have shown and large-scale tests have confirmed that metal electroplating and 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 (of course, the economic estimates presented in the quoted references need to updated to current time). 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 practice.

The major difference between the unit operations described in this document and more conventional treatment is that we based the sequential treatment primarily on metal value precipitation of metal phosphates.

SUMMARY OF REPORTS SUBMITED TO EPA (Abstracts and Conclusions Included)

Treatment of Electroplating Hydroxide Sludge Materials

1. Twidwell, L.G., November 1984. *Metal Value Recovery from Metal Hydroxide Sludges*. EPA R-809 305 01, R-81-73601, November, 491p; First year draft report is also available **Twidwell, L.G., J. Archibald, November 1983.** *Metal Value Recovery from Metal Hydroxide Sludges.* Montana Tech Foundation, Montana College of Mineral Science and Technology, Butte Montana. 285p.

Abstract {Twidwell, L.G., November 1984 Report)

A two-year study investigating the potential for metal value recovery from metal hydroxide sludges has been completed. The objectives of the study were:

- Develop a flowsheet to separate and recover metal values from metal finishing hydroxide sludge materials.
- Develop a test assembly of unit operations to accomplish the separation of metal values on a scale of 75-100 pounds of sludge per day
- Verify that the large-scale unit operations accomplish appropriate separations, and
- Delineate potential operational problems.

The results of the first phase research successfully accomplished the required objectives. Flowsheets were designed and tested on a laboratory scale prior to full-scale testing. The flowsheets consist of: sulfuric acid leaching; iron removal by jarosite precipitation (high iron bearing solutions) or iron solvent extraction (low iron bearing solutions) [both treatments later replaced by iron phosphate precipitation]; copper removal by solvent extraction and copper recovery by either electrowinning or copper sulfate crystallization; zinc removal by solvent event extraction and zinc recovery as zinc sulfate by crystallization; chromium oxidation and subsequent recovery by lead chromate precipitation [later replaced by chromium phosphate precipitation]; nickel removal by sulfide precipitation of nickel sulfate crystallization precipitation [later replaced by nickel phosphate precipitation]; and, final solution clean-up of low concentration residual ions by ion exchange.

Full scale tests have been performed to ascertain the applicability of each unit operation. Continuous tests have been performed to investigate solvent reagent degradation; to develop mass balances; and to delineate operational problems. The successful application of metallurgical unit operations to multi-component complex mixed metal sludges has demonstrated treatment of such material is possible and economical.

This report covered the period: July 1, 1982 to September 30, 1983. [later studies demonstrated that a simplified treatment can be used based on phosphate precipitation unit operations, see the report.

Brief Conclusions

The conclusions for the Laboratory Test Program are too voluminous to include here. Please refer to **Twidwell, L.G., November 1984 Report** Section 2; 2.1 Laboratory Test Program; pages 5 to 7 and Section 2; 2.1 Large Scale Test Program; pages 7-16.

The flowsheet that resulted from the Phase I study was based on the treatment of a mixed metal sludge material produced from electroplating production operations. Two types of hydroxide sludge materials have been considered in this series of studies for EPA, i.e., hydroxide sludge from **electroplating** and sludges generated during **electromachining operations**. The Phase I study considered the **electroplating hydroxide materials** and is discussed in this referenced publication.

The flowsheet for treating the electroplating materials contained significant concentrations of metals values: copper, nickel, zinc, and chromium and variable concentrations of other elements that were not considered recoverable as marketable products but which required removal in order not to contaminate the metal value products, e.g., iron, aluminum, and calcium.

An important point concerning the development of the treatment sequence is that only commercial process unit operations and commonly used reagents were considered. New developments in the separation of metals from complex.

As an example of the sequential treatment used in this study, a flowsheet summarizing the large scale sequential experimental study is illustrated in Figure 6.1 pages 37 to 43 and Tables 6.1 to 6.3, pages 44 to 46 (The flowsheet shown was reported in the **Twidwell, L.G., J. Archibald 1983 Report).** [A similar flowsheet was presented in the **Twidwell, L.G., November 1984 Report,** pages 75 to 80].

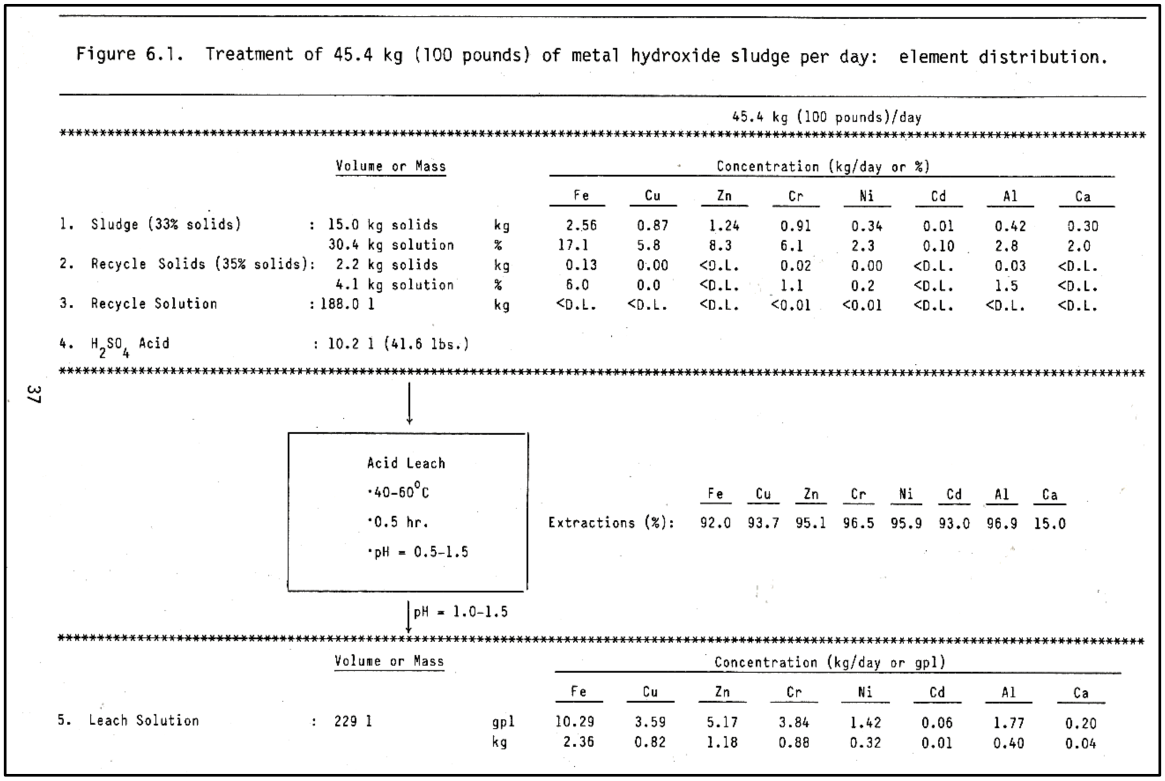

Figure 6.1. Treatment of 45.4 kg (100 pounds) of metal hydroxide sludge per day: element distribution.

45.4 kg (100 pounds)/day

	Volume or Mass		Concentration (kg/day or %)							
			Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
1. Sludge (33% solids)	: 15.0 kg solids	kg	2.56	0.87	1.24	0.91	0.34	0.01	0.42	0.30
	30.4 kg solution	%	17.1	5.8	8.3	6.1	2.3	0.10	2.8	2.0
2. Recycle Solids (35% solids):	2.2 kg solids	kg	0.13	0.00	<D.L.	0.02	0.00	<D.L.	0.03	<D.L.
	4.1 kg solution	%	6.0	0.0	<D.L.	1.1	0.2	<D.L.	1.5	<D.L.
3. Recycle Solution	: 188.0 l	kg	<D.L.	<D.L.	<D.L.	<0.01	<0.01	<D.L.	<D.L.	<D.L.
4. H_2SO_4 Acid	: 10.2 l (41.6 lbs.)									

Acid Leach
- 40-60°C
- 0.5 hr.
- pH = 0.5-1.5

	Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
Extractions (%):	92.0	93.7	95.1	96.5	95.9	93.0	96.9	15.0

pH = 1.0-1.5

	Volume or Mass		Concentration (kg/day or gpl)							
			Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
5. Leach Solution	: 229 l	gpl	10.29	3.59	5.17	3.84	1.42	0.06	1.77	0.20
		kg	2.36	0.82	1.18	0.88	0.32	0.01	0.40	0.04

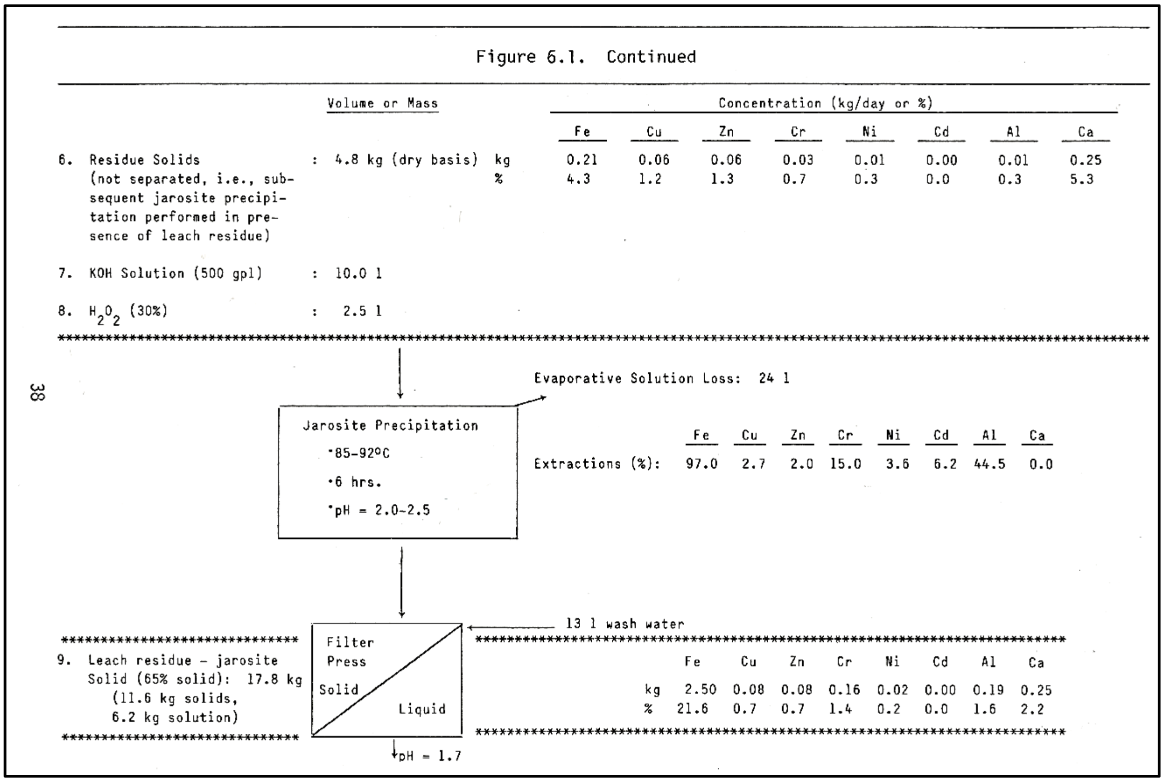

Figure 6.1. Continued

	Volume or Mass		Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
			Concentration (kg/day or %)							
6. Residue Solids (not separated, i.e., subsequent jarosite precipitation performed in presence of leach residue)	: 4.8 kg (dry basis)	kg	0.21	0.06	0.06	0.03	0.01	0.00	0.01	0.25
		%	4.3	1.2	1.3	0.7	0.3	0.0	0.3	5.3
7. KOH Solution (500 gpl)	: 10.0 l									
8. H_2O_2 (30%)	: 2.5 l									

Evaporative Solution Loss: 24 l

Jarosite Precipitation
- 85-92°C
- 6 hrs.
- pH = 2.0-2.5

	Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
Extractions (%):	97.0	2.7	2.0	15.0	3.6	6.2	44.5	0.0

13 l wash water

Filter Press

Solid

Liquid

9. Leach residue - jarosite
Solid (65% solid): 17.8 kg
(11.6 kg solids,
6.2 kg solution)

	Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
kg	2.50	0.08	0.08	0.16	0.02	0.00	0.19	0.25
%	21.6	0.7	0.7	1.4	0.2	0.0	1.6	2.2

pH = 1.7

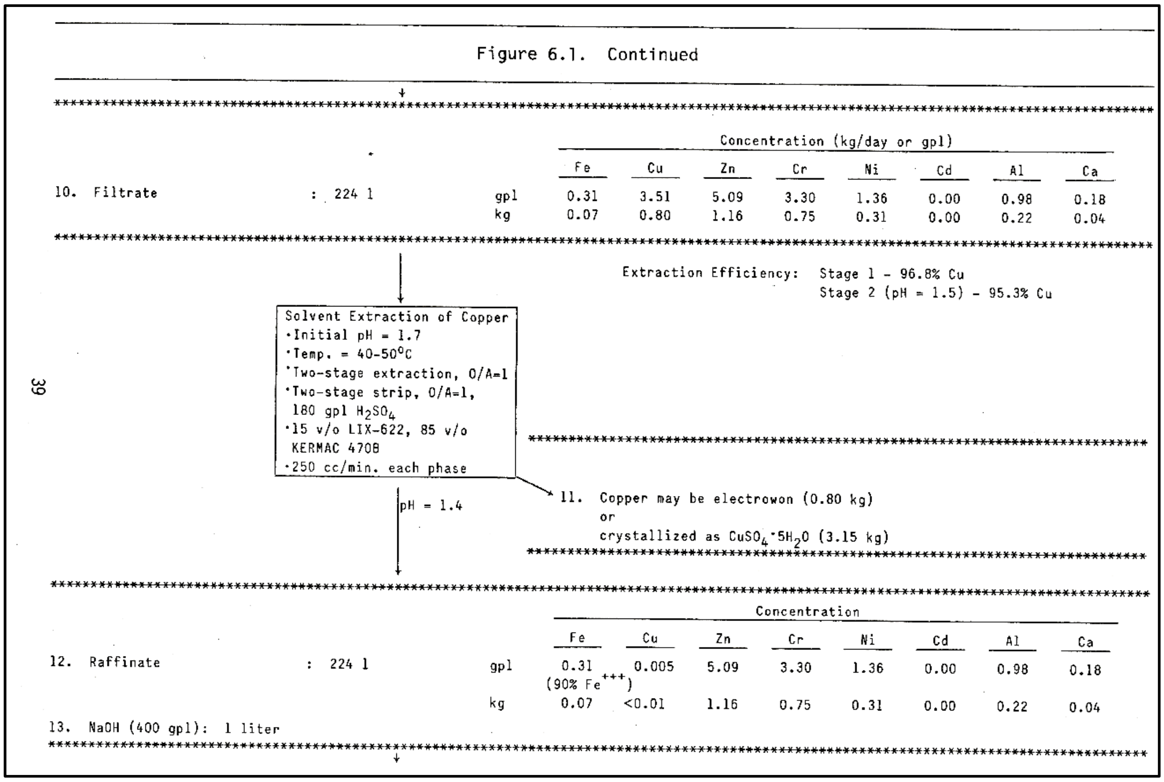

Figure 6.1. Continued

			Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
			Concentration (kg/day or gpl)							
10. Filtrate	: 224 l	gpl	0.31	3.51	5.09	3.30	1.36	0.00	0.98	0.18
		kg	0.07	0.80	1.16	0.75	0.31	0.00	0.22	0.04

Extraction Efficiency: Stage 1 - 96.8% Cu
Stage 2 (pH = 1.5) - 95.3% Cu

Solvent Extraction of Copper
- Initial pH = 1.7
- Temp. = 40-50°C
- Two-stage extraction, O/A=1
- Two-stage strip, O/A=1, 180 gpl H_2SO_4
- 15 v/o LIX-622, 85 v/o KERMAC 470B
- 250 cc/min. each phase

11. Copper may be electrowon (0.80 kg)
or
crystallized as $CuSO_4 \cdot 5H_2O$ (3.15 kg)

pH = 1.4

			Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
			Concentration							
12. Raffinate	: 224 l	gpl	0.31 (90% Fe^{+++})	0.005	5.09	3.30	1.36	0.00	0.98	0.18
		kg	0.07	<0.01	1.16	0.75	0.31	0.00	0.22	0.04

13. NaOH (400 gpl): 1 liter

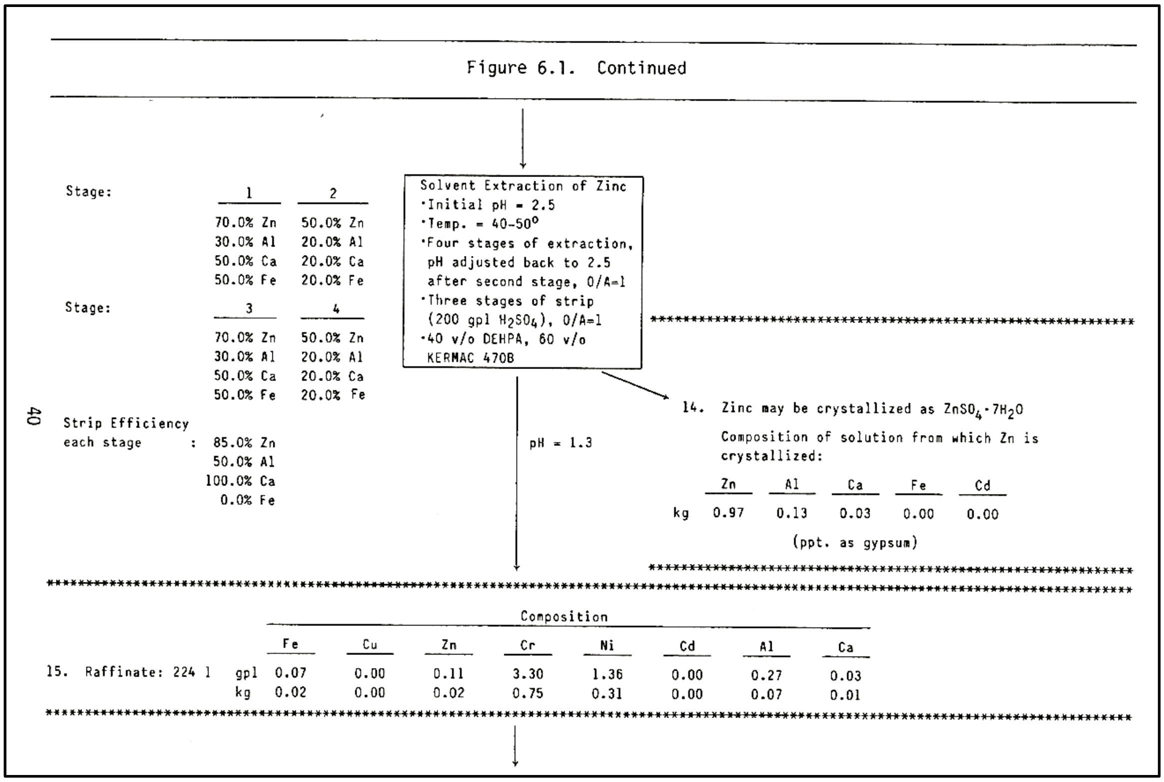

Figure 6.1. Continued

Solvent Extraction of Zinc
- Initial pH = 2.5
- Temp. = 40-50°
- Four stages of extraction, pH adjusted back to 2.5 after second stage, O/A=1
- Three stages of strip (200 gpl H_2SO_4), O/A=1
- 40 v/o DEHPA, 60 v/o KERMAC 470B

Stage:	1	2
	70.0% Zn	50.0% Zn
	30.0% Al	20.0% Al
	50.0% Ca	20.0% Ca
	50.0% Fe	20.0% Fe

Stage:	3	4
	70.0% Zn	50.0% Zn
	30.0% Al	20.0% Al
	50.0% Ca	20.0% Ca
	50.0% Fe	20.0% Fe

Strip Efficiency each stage : 85.0% Zn
50.0% Al
100.0% Ca
0.0% Fe

pH = 1.3

14. Zinc may be crystallized as $ZnSO_4 \cdot 7H_2O$

Composition of solution from which Zn is crystallized:

	Zn	Al	Ca	Fe	Cd
kg	0.97	0.13	0.03	0.00	0.00

(ppt. as gypsum)

		Composition							
		Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
15. Raffinate: 224 l	gpl	0.07	0.00	0.11	3.30	1.36	0.00	0.27	0.03
	kg	0.02	0.00	0.02	0.75	0.31	0.00	0.07	0.01

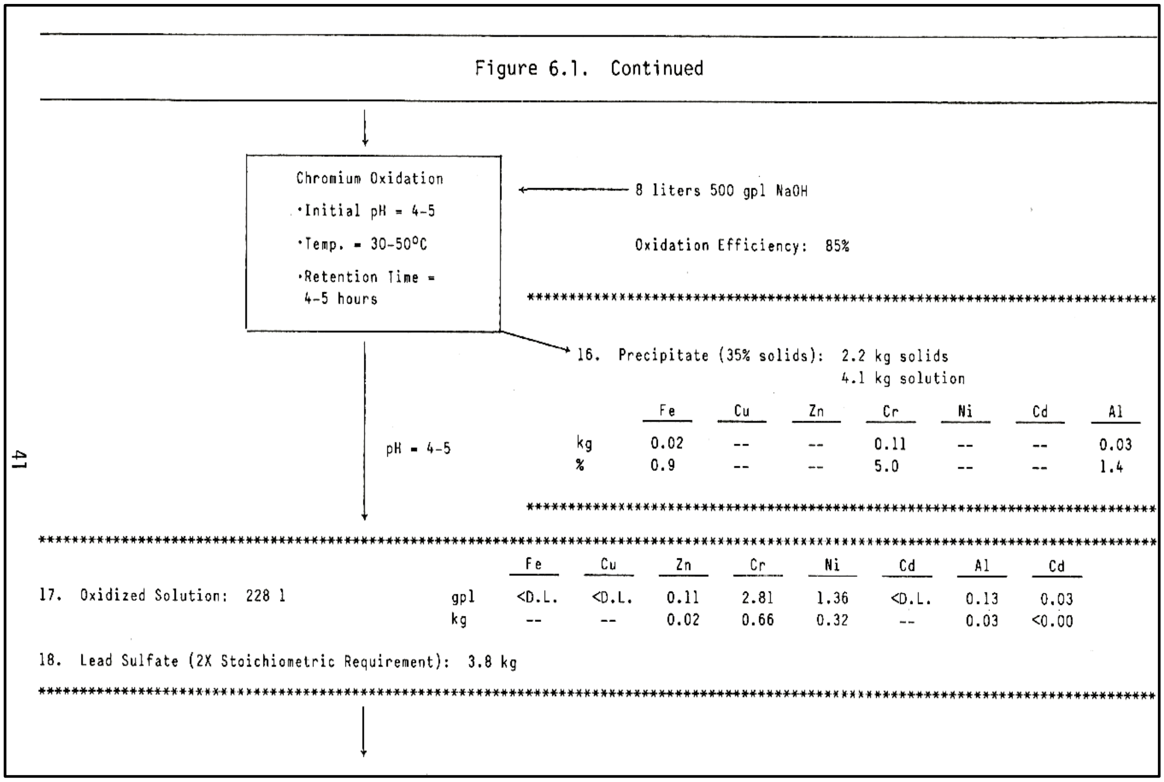

Figure 6.1. Continued

Chromium Oxidation
- Initial pH = 4-5
- Temp. = 30-50°C
- Retention Time = 4-5 hours

← 8 liters 500 gpl NaOH

Oxidation Efficiency: 85%

16. Precipitate (35% solids): 2.2 kg solids
4.1 kg solution

	Fe	Cu	Zn	Cr	Ni	Cd	Al
kg	0.02	--	--	0.11	--	--	0.03
%	0.9	--	--	5.0	--	--	1.4

pH = 4-5

		Fe	Cu	Zn	Cr	Ni	Cd	Al	Cd
17. Oxidized Solution: 228 l	gpl	<D.L.	<D.L.	0.11	2.81	1.36	<D.L.	0.13	0.03
	kg	--	--	0.02	0.66	0.32	--	0.03	<0.00

18. Lead Sulfate (2X Stoichiometric Requirement): 3.8 kg

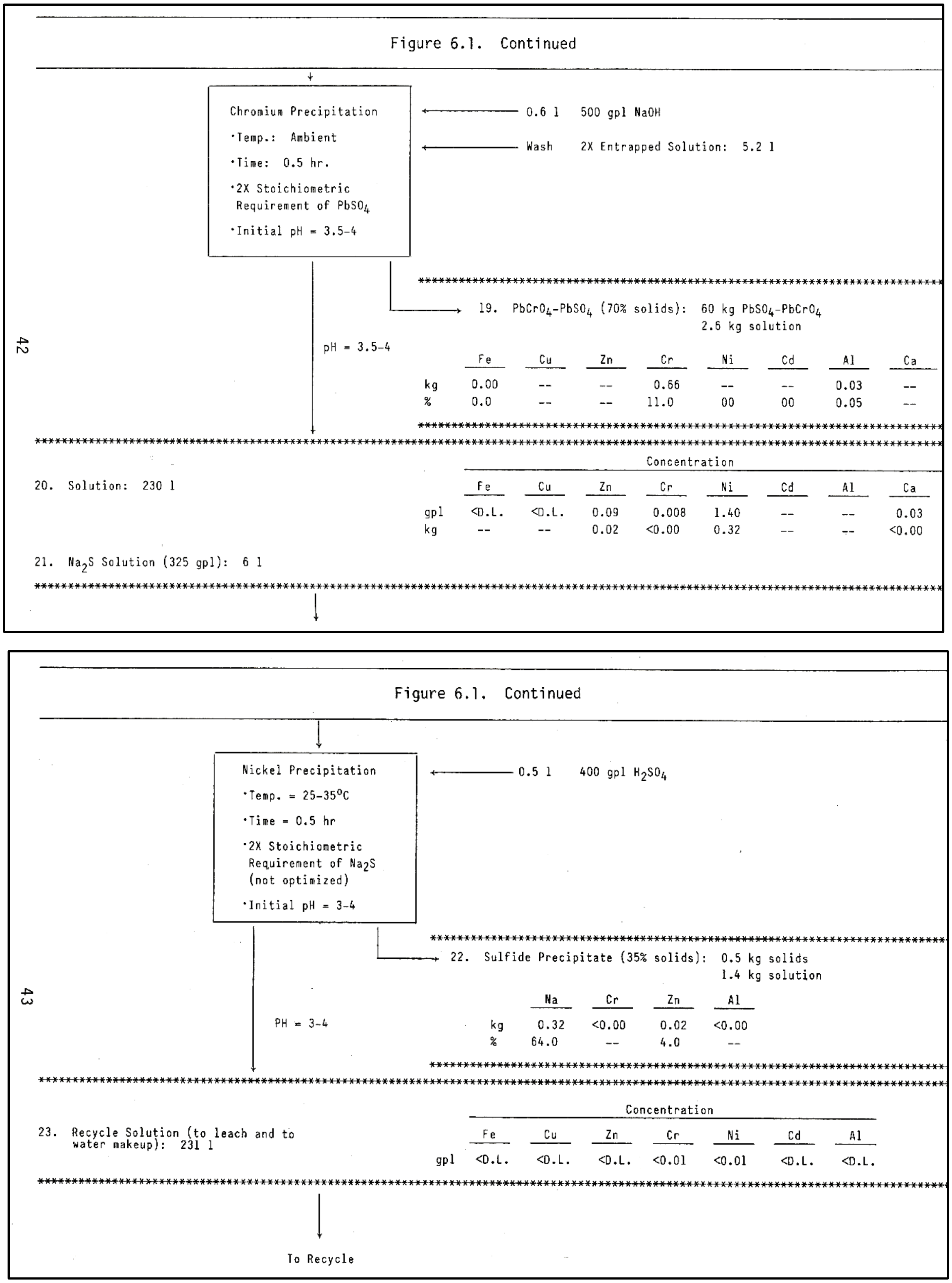

Figure 6.1. Continued

Chromium Precipitation
- Temp.: Ambient
- Time: 0.5 hr.
- 2X Stoichiometric Requirement of $PbSO_4$
- Initial pH = 3.5-4

← 0.6 l 500 gpl NaOH

← Wash 2X Entrapped Solution: 5.2 l

pH = 3.5-4

19. $PbCrO_4$-$PbSO_4$ (70% solids): 60 kg $PbSO_4$-$PbCrO_4$
2.6 kg solution

	Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
kg	0.00	--	--	0.66	--	--	0.03	--
%	0.0	--	--	11.0	00	00	0.05	--

20. Solution: 230 l

	Concentration							
	Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
gpl	<D.L.	<D.L.	0.09	0.008	1.40	--	--	0.03
kg	--	--	0.02	<0.00	0.32	--	--	<0.00

21. Na_2S Solution (325 gpl): 6 l

Figure 6.1. Continued

Nickel Precipitation
- Temp. = 25-35°C
- Time = 0.5 hr
- 2X Stoichiometric Requirement of Na_2S (not optimized)
- Initial pH = 3-4

← 0.5 l 400 gpl H_2SO_4

PH = 3-4

22. Sulfide Precipitate (35% solids): 0.5 kg solids
1.4 kg solution

	Na	Cr	Zn	Al
kg	0.32	<0.00	0.02	<0.00
%	64.0	--	4.0	--

23. Recycle Solution (to leach and to water makeup): 231 l

	Concentration						
	Fe	Cu	Zn	Cr	Ni	Cd	Al
gpl	<D.L.	<D.L.	<D.L.	<0.01	<0.01	<D.L.	<D.L.

To Recycle

Figure 10. Treatment of 45.4 kg of metal hydroxide sludge per day: element distribution (Figure 6.1 in the Twidwell, L.G, J. Archibald Report, November 1983, Pages 37 to 43)

Table 2. Treatment of metal hydroxide sludge: element distribution summary (Table 6.1 in the Twidwell, L.G and J. Archibald Report, November 1983, page 44)

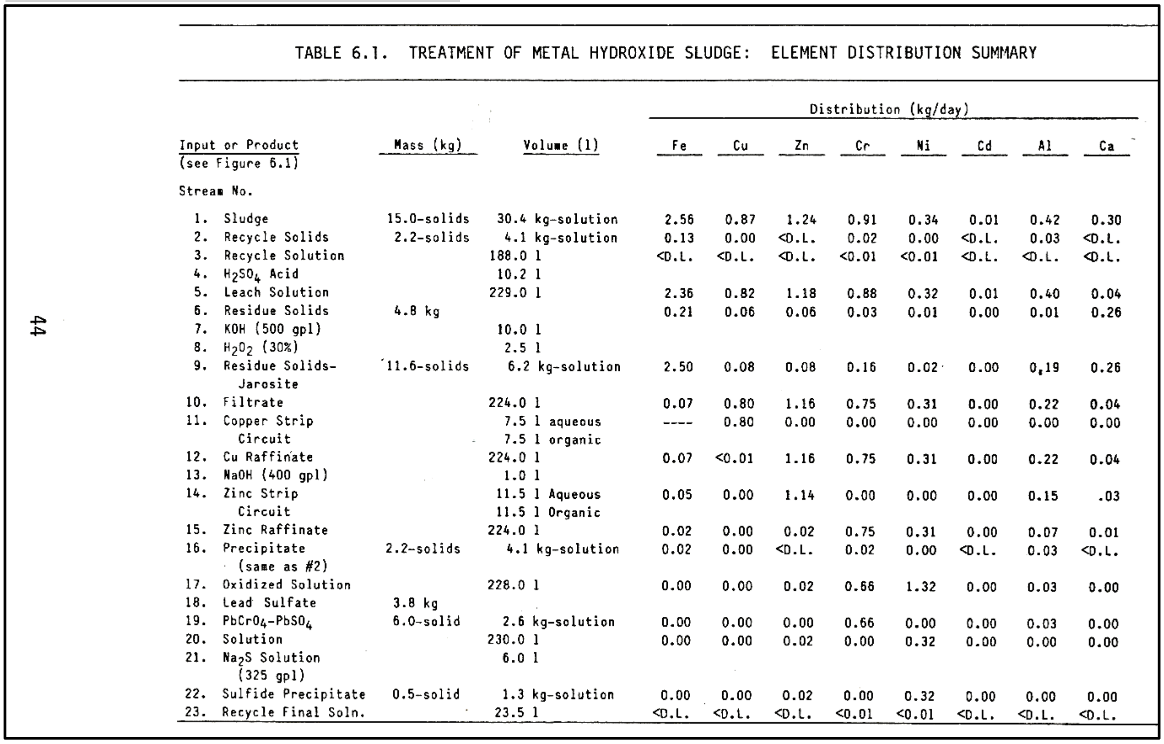

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TABLE 6.1. TREATMENT OF METAL HYDROXIDE SLUDGE: ELEMENT DISTRIBUTION SUMMARY

Input or Product (see Figure 6.1)	Mass (kg)	Volume (l)	Distribution (kg/day) Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
Stream No.										
1. Sludge	15.0-solids	30.4 kg-solution	2.56	0.87	1.24	0.91	0.34	0.01	0.42	0.30
2. Recycle Solids	2.2-solids	4.1 kg-solution	0.13	0.00	<D.L.	0.02	0.00	<D.L.	0.03	<D.L.
3. Recycle Solution		188.0 l	<D.L.	<D.L.	<D.L.	<0.01	<0.01	<D.L.	<D.L.	<D.L.
4. H_2SO_4 Acid		10.2 l								
5. Leach Solution		229.0 l	2.36	0.82	1.18	0.88	0.32	0.01	0.40	0.04
6. Residue Solids	4.8 kg		0.21	0.06	0.06	0.03	0.01	0.00	0.01	0.26
7. KOH (500 gpl)		10.0 l								
8. H_2O_2 (30%)		2.5 l								
9. Residue Solids-Jarosite	11.6-solids	6.2 kg-solution	2.50	0.08	0.08	0.16	0.02	0.00	0.19	0.26
10. Filtrate		224.0 l	0.07	0.80	1.16	0.75	0.31	0.00	0.22	0.04
11. Copper Strip Circuit		7.5 l aqueous 7.5 l organic	----	0.80	0.00	0.00	0.00	0.00	0.00	0.00
12. Cu Raffinate		224.0 l	0.07	<0.01	1.16	0.75	0.31	0.00	0.22	0.04
13. NaOH (400 gpl)		1.0 l								
14. Zinc Strip Circuit		11.5 l Aqueous 11.5 l Organic	0.05	0.00	1.14	0.00	0.00	0.00	0.15	.03
15. Zinc Raffinate		224.0 l	0.02	0.00	0.02	0.75	0.31	0.00	0.07	0.01
16. Precipitate (same as #2)	2.2-solids	4.1 kg-solution	0.02	0.00	<D.L.	0.02	0.00	<D.L.	0.03	<D.L.
17. Oxidized Solution		228.0 l	0.00	0.00	0.02	0.66	1.32	0.00	0.03	0.00
18. Lead Sulfate	3.8 kg									
19. $PbCrO_4$-$PbSO_4$	6.0-solid	2.6 kg-solution	0.00	0.00	0.00	0.66	0.00	0.00	0.03	0.00
20. Solution		230.0 l	0.00	0.00	0.02	0.00	0.32	0.00	0.00	0.00
21. Na_2S Solution (325 gpl)		6.0 l								
22. Sulfide Precipitate	0.5-solid	1.3 kg-solution	0.00	0.00	0.02	0.00	0.32	0.00	0.00	0.00
23. Recycle Final Soln.		23.5 l	<D.L.	<D.L.	<D.L.	<0.01	<0.01	<D.L.	<D.L.	<D.L.

Table 3. Treatment of metal hydroxide sludge: distribution of specific products (Table 6.2 in the Twidwell, L.G, J. Archibald Report, November 1983, Page 45)

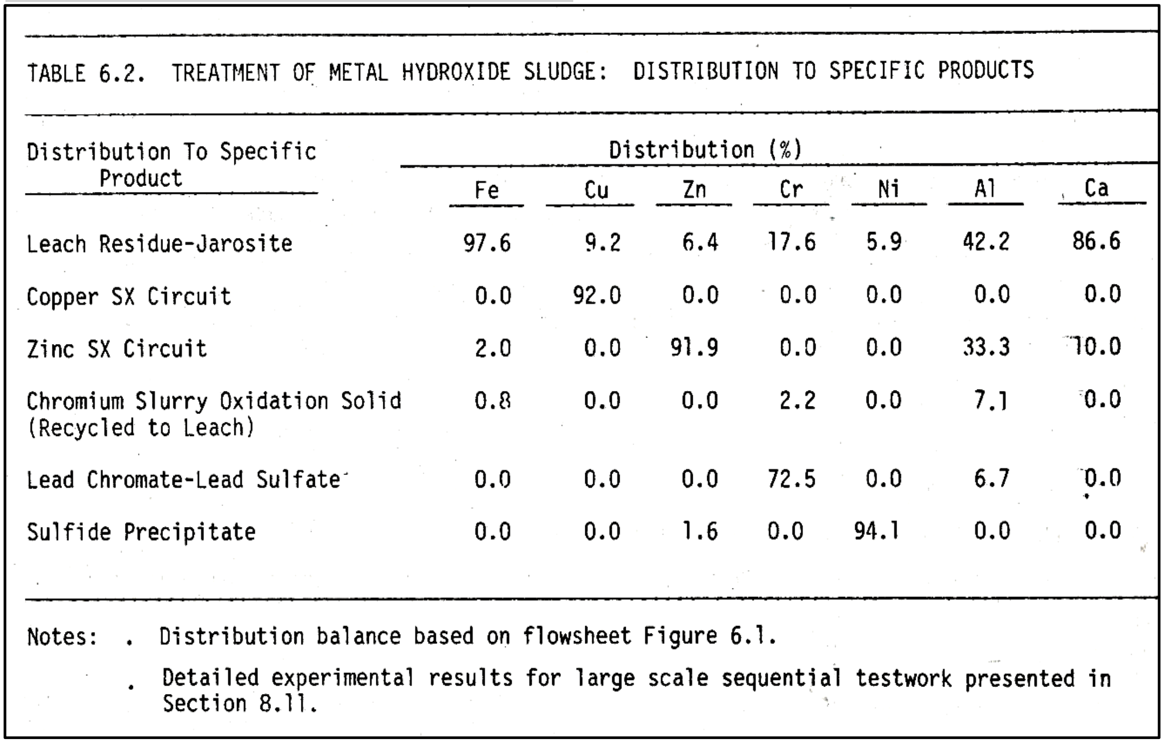


TABLE 6.2. TREATMENT OF METAL HYDROXIDE SLUDGE: DISTRIBUTION TO SPECIFIC PRODUCTS

Distribution To Specific Product	Distribution (%) Fe	Cu	Zn	Cr	Ni	Al	Ca
Leach Residue-Jarosite	97.6	9.2	6.4	17.6	5.9	42.2	86.6
Copper SX Circuit	0.0	92.0	0.0	0.0	0.0	0.0	0.0
Zinc SX Circuit	2.0	0.0	91.9	0.0	0.0	33.3	10.0
Chromium Slurry Oxidation Solid (Recycled to Leach)	0.8	0.0	0.0	2.2	0.0	7.1	0.0
Lead Chromate-Lead Sulfate	0.0	0.0	0.0	72.5	0.0	6.7	0.0
Sulfide Precipitate	0.0	0.0	1.6	0.0	94.1	0.0	0.0

Notes:
- Distribution balance based on flowsheet Figure 6.1.
- Detailed experimental results for large scale sequential testwork presented in Section 8.11.

Table 4. Treatment of metal hydroxide sludge: Element content in solid products (Table 6.3 in the Twidwell, L.G, J. Archibald Report, November 1983, page 46)

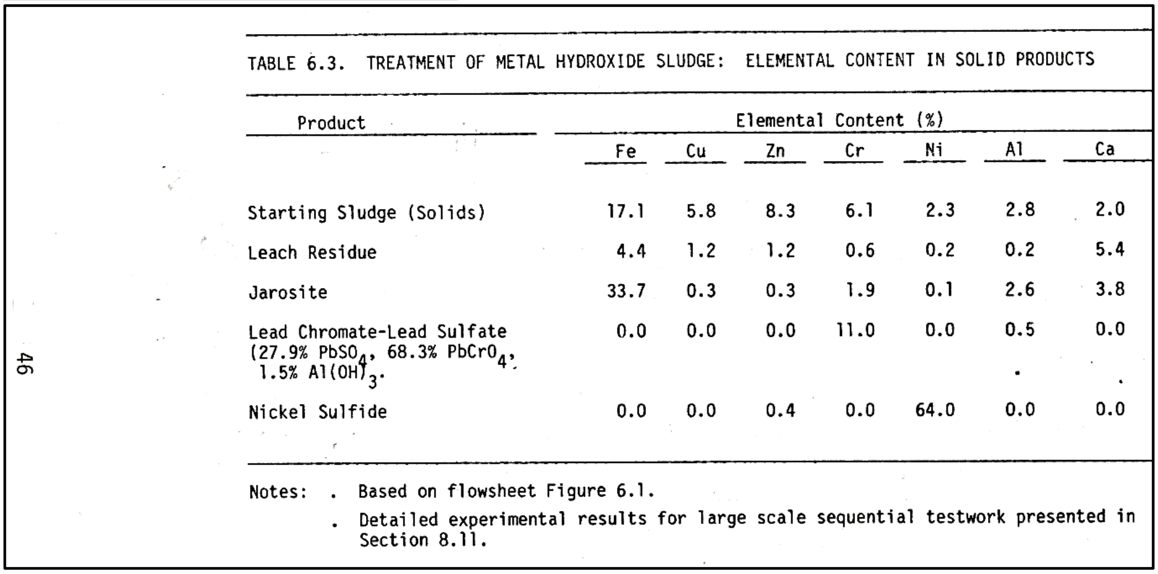


TABLE 6.3. TREATMENT OF METAL HYDROXIDE SLUDGE: ELEMENTAL CONTENT IN SOLID PRODUCTS

Product	Elemental Content (%)						
	Fe	Cu	Zn	Cr	Ni	Al	Ca
Starting Sludge (Solids)	17.1	5.8	8.3	6.1	2.3	2.8	2.0
Leach Residue	4.4	1.2	1.2	0.6	0.2	0.2	5.4
Jarosite	33.7	0.3	0.3	1.9	0.1	2.6	3.8
Lead Chromate-Lead Sulfate (27.9% $PbSO_4$, 68.3% $PbCrO_4$, 1.5% $Al(OH)_3$.	0.0	0.0	0.0	11.0	0.0	0.5	0.0
Nickel Sulfide	0.0	0.0	0.4	0.0	64.0	0.0	0.0

Notes:
- Based on flowsheet Figure 6.1.
- Detailed experimental results for large scale sequential testwork presented in Section 8.11.

2. Twidwell, L.G., D.R. Dahnke Report, July 1987. *Metal Value Recovery from Metal Hydroxide Sludges*: *Removal of Iron and Recovery of Chromium*. EPA CR-812533-01-0 July, 202p, EPA-HWRL, Final Report to EPA, Cincinnati, OH, Montana Enviromet, Inc., Butte, MT.

Abstract

The objectives of this study were to develop flowsheets to separate and recover metal values from **electrochemical machining** hydroxide sludge materials; collect bench scale experimental data to verify the feasibility of the proposed flowsheets; and to develop a first order economic evaluation of the potential flowsheets. The major differences electroplating and electromachining sludge materials was that the electromachining materials contained more valuable constituent metals, i.e., higher chromium, nickel and in some cases cobalt (but much lower concentrations of iron). The present study was conduced on sludge supplied by a nationally known electromachining company. A typical nominal composition (in %) was iron (8), chromium (6); Ni (18); and, cobalt (1). However, the focus of the studies reported in this study was the separation of iron and chromium as metal phosphates.

These above stated objectives of the study were accomplished. Flowsheets and alternatives are discussed in the body of the report. The developed flowsheets have been verified to be feasible by laboratory test work. Selective metal value separations have been shown to be possible utilizing phosphate chemistry, e.g., iron can be recovered as ferric phosphate or ferric oxide; cobalt can be recovered as cobaltous phosphate, cobaltous hydroxide, or cobaltic oxide; nickel can be recovered as nickel phosphate or nickel sulfate or nickel sulfide; and chromium as chromium phosphate, chromic acid, or chromium oxide.

Brief Conclusions

The conclusions for the Laboratory Test Program are too voluminous to include here. Please refer to **Twidwell, L.G., D.R. Dahnke Report, July 1987** Section 6 and 6.1: Laboratory Test Program; pages 37 to 52.

An example flowsheet for the separation of iron, chromium, zinc (8000 gm large scale test program performed on LEHR sludge) is presented in Figure 6.41 (page 124) and Tables 6.20 and 6.21. Similar studies were conducted for the iron, chromium, nickel, cobalt, etc.

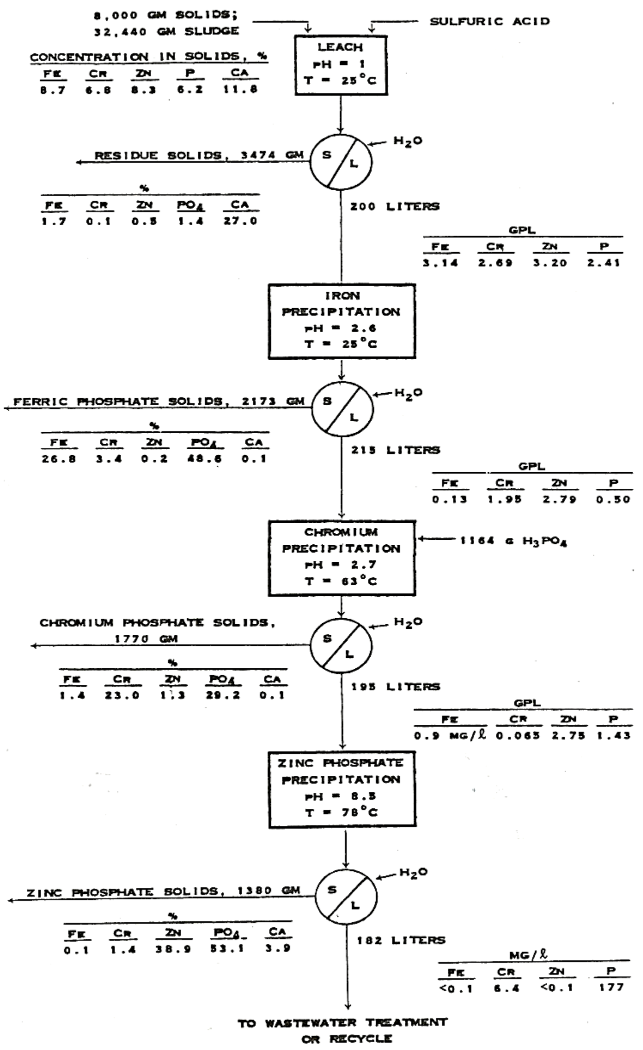


FIGURE 6.41. FLOWSHEET FOR THE SEPARATION OF FE-CR-ZN BY PHOSPHATE PRECIPITATION.

Figure 11. Flowsheet for the separation of Fe-Ca-Zn by phosphate precipitation [Figure 6.41 in the Twidwell, L.G., D.R. Dahnke Report, July 1987, page 124]

Table 5. Products from the Fe-Cr-Zn large scale test (Table 6.20 in the Twidwell, L.G., D.R. Dahnke Report, July 1987, page 125)

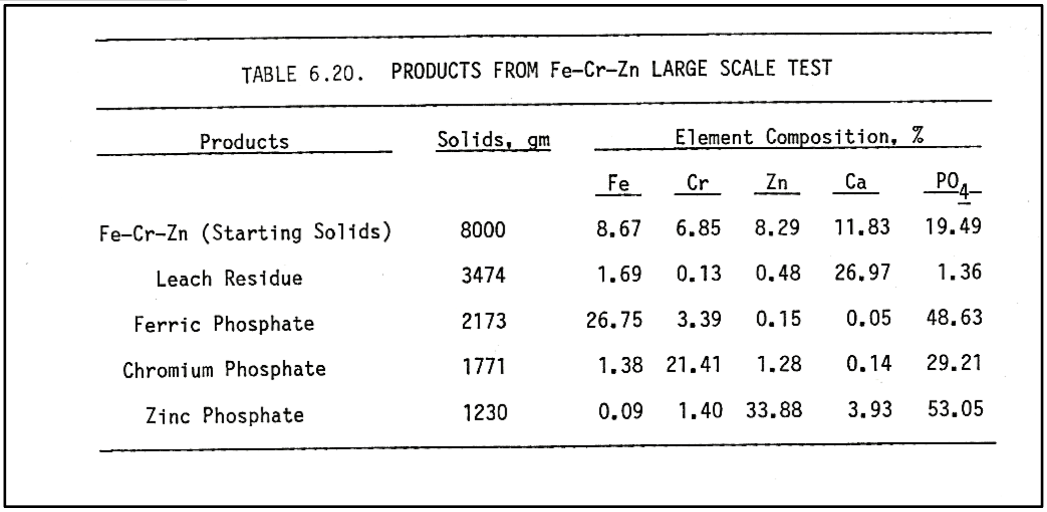


TABLE 6.20. PRODUCTS FROM Fe-Cr-Zn LARGE SCALE TEST

Products	Solids, gm	Element Composition, %				
		Fe	Cr	Zn	Ca	PO_4
Fe-Cr-Zn (Starting Solids)	8000	8.67	6.85	8.29	11.83	19.49
Leach Residue	3474	1.69	0.13	0.48	26.97	1.36
Ferric Phosphate	2173	26.75	3.39	0.15	0.05	48.63
Chromium Phosphate	1771	1.38	21.41	1.28	0.14	29.21
Zinc Phosphate	1230	0.09	1.40	33.88	3.93	53.05

Table 6. EP Toxicity test (Table 6.21 in the Twidwell, L.G., D.R. Dahnke Report July 1987, Page 126)

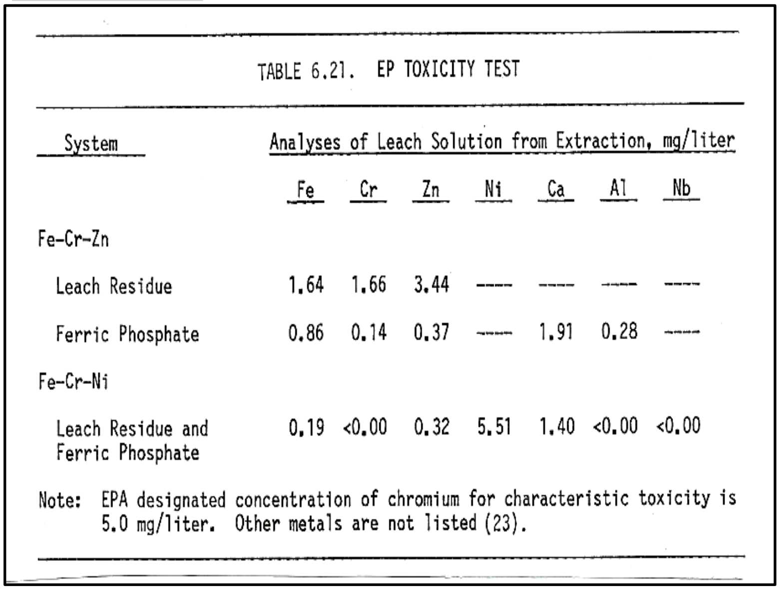


TABLE 6.21. EP TOXICITY TEST

System	Analyses of Leach Solution from Extraction, mg/liter						
	Fe	Cr	Zn	Ni	Ca	Al	Nb
Fe-Cr-Zn							
Leach Residue	1.64	1.66	3.44	----	----	----	----
Ferric Phosphate	0.86	0.14	0.37	----	1.91	0.28	----
Fe-Cr-Ni							
Leach Residue and Ferric Phosphate	0.19	<0.00	0.32	5.51	1.40	<0.00	<0.00

Note: EPA designated concentration of chromium for characteristic toxicity is 5.0 mg/liter. Other metals are not listed (23).

3. **Twidwell, L.G., D.R. Dahnke Report, March 1986.** *Metal Value Recovery from Alloy Chemical Milling Waste:* EPA Contract Number 68-02-4172. March, 184p. **Twidwell, L.G., D.R. Dahnke, December 1987,** *Metal Value Recovery from Alloy Chemical Milling Waste: Phase II.* EPA Contract Number 68-02-4432. December, 189p.

Abstract (1986)

The objectives of these studies were to develop flowsheets to separate and recover metal values from high value **electrochemical machining** hydroxide sludge materials; collect bench scale experimental data to verify the feasibility of the proposed flowsheets; and to develop a first order economic evaluation of the potential flowsheets.

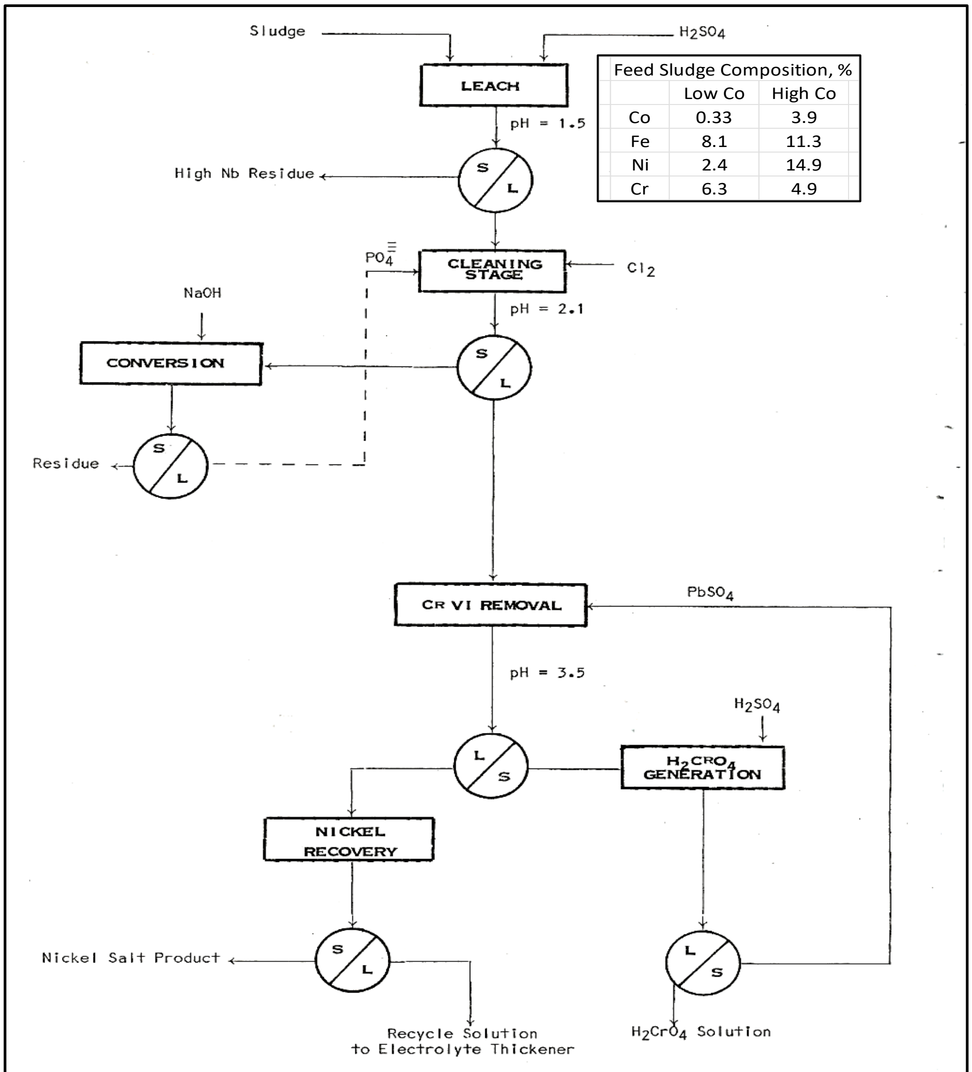
These objectives have been accomplished. Flowsheets and alternatives are discussed in the body of the reports. The developed flowsheets have been verified to be feasible by laboratory test work. Selective metal value separations have been shown to be possible, e.g., iron can be recovered as ferric phosphate or ferric oxide; cobalt can be recovered as cobaltous phosphate, cobaltous hydroxide, cobaltic oxide or metallic cobalt; nickel can be recovered as nickel sulfate, or metallic nickel; and chromium as chromium phosphate, chromic acid, or chromium oxide.

Two concepts were investigated for the high purity separation of nickel and cobalt, e.g., (1) the use of dimethylglyoxime (DMG) to selectively precipitate nickel from cobalt and (2) the formation of a double-salt selective precipitation of nickel from cobalt. The DMG approach was the focus of the present studies. A separate study focused on the separation of nickel and cobalt using an adaptation of the Liebig analytical procedure to precipitate nickelic hydroxide and dissolve the cobalt as a cyanide double-salt with subsequent conversion to cobaltic oxide.

Brief Conclusions

The conclusions for the Laboratory Test Program are too voluminous to include here. Please refer to Phase 1 Report (**Twidwell, L.G., D.R. Dahnke Report, March 1986),** Section 2; 2.1 Laboratory Test Program; pages 5 to 9 or Phase 2 Report (**Twidwell, L.G., D.R. Dahnke Report, December 1987),** Section 2; 2.1 Laboratory Test Program; pages 16 to 24.

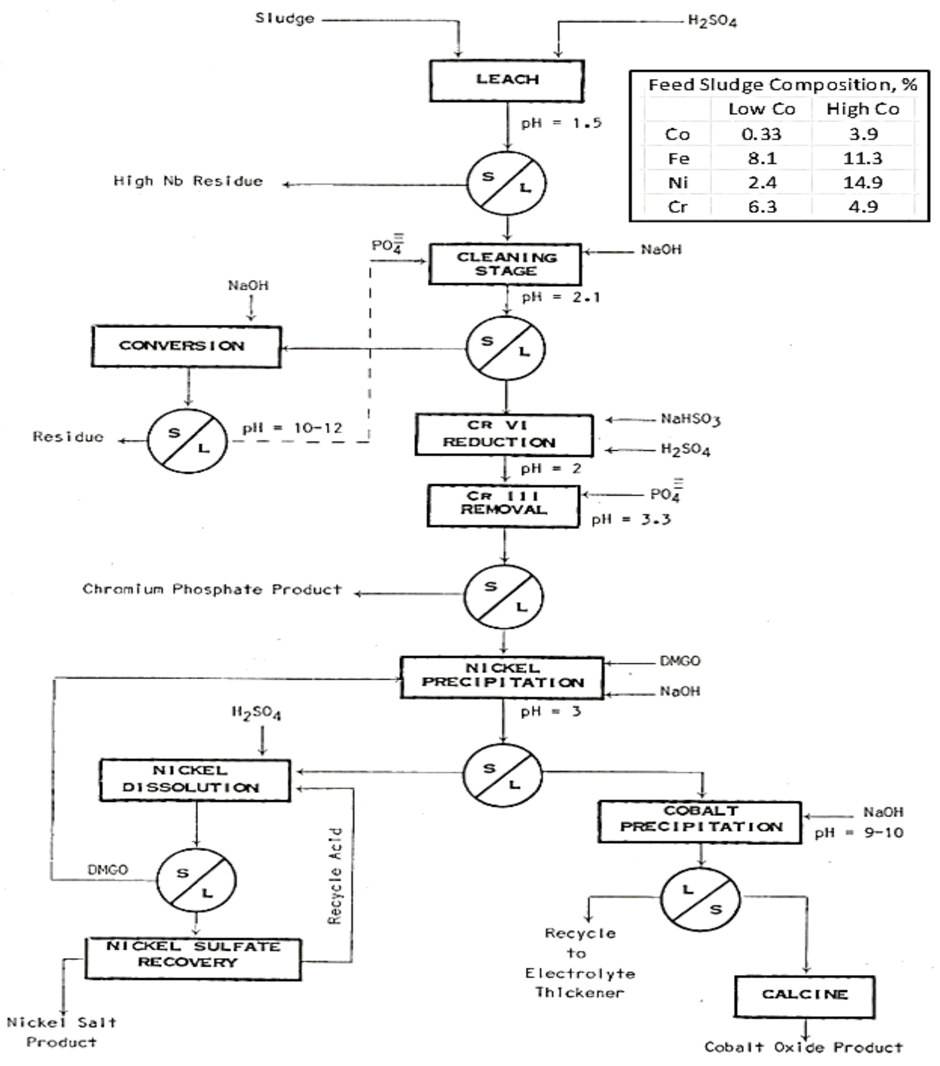
Example flowsheets are presented in (**Twidwell, L.G., D.R. Dahnke Report, March 1986),** Figures 12 [Figure 2.1 [Low Cobalt, page 6) and Figure 13 [Figure 2.2 (High Cobalt, page 7]. The separation of nickel selectively from cobalt is via precipitation of nickel dimethylglyoxime (DMG). Also, a flowsheet Figure 14 (**Twidwell, L.G., D.R. Dahnke Report, December 1987** [Figure 6.27, pages 142 to 145**)** for treating 10 tons/day of high cobalt (3.9%) electromachining sludge.**)**



Feed Sludge Composition, %		
	Low Co	High Co
Co	0.33	3.9
Fe	8.1	11.3
Ni	2.4	14.9
Cr	6.3	4.9

FIGURE 2.1. FLOWSHEET FOR THE TREATMENT OF LOW COBALT BEARING ECM SLUDGE (ECM 1).

Figure 12. Flowsheet for the treatment of low cobalt bearing ECM sludge (Figure 2.1 in the Twidwell, L.G., D.R. Dahnke Report, March 1986, page 6)



Feed Sludge Composition, %		
	Low Co	High Co
Co	0.33	3.9
Fe	8.1	11.3
Ni	2.4	14.9
Cr	6.3	4.9

FIGURE 2.2. FLOWSHEET FOR THE TREATMENT OF HIGH COBALT BEARING ECM SLUDGES.

Figure 13. Flowsheet for the treatment of high cobalt bearing ECM sludge (Figure 2.2 in the Twidwell, L.G., D.R. Dahnke Report, March 1986, page 7)

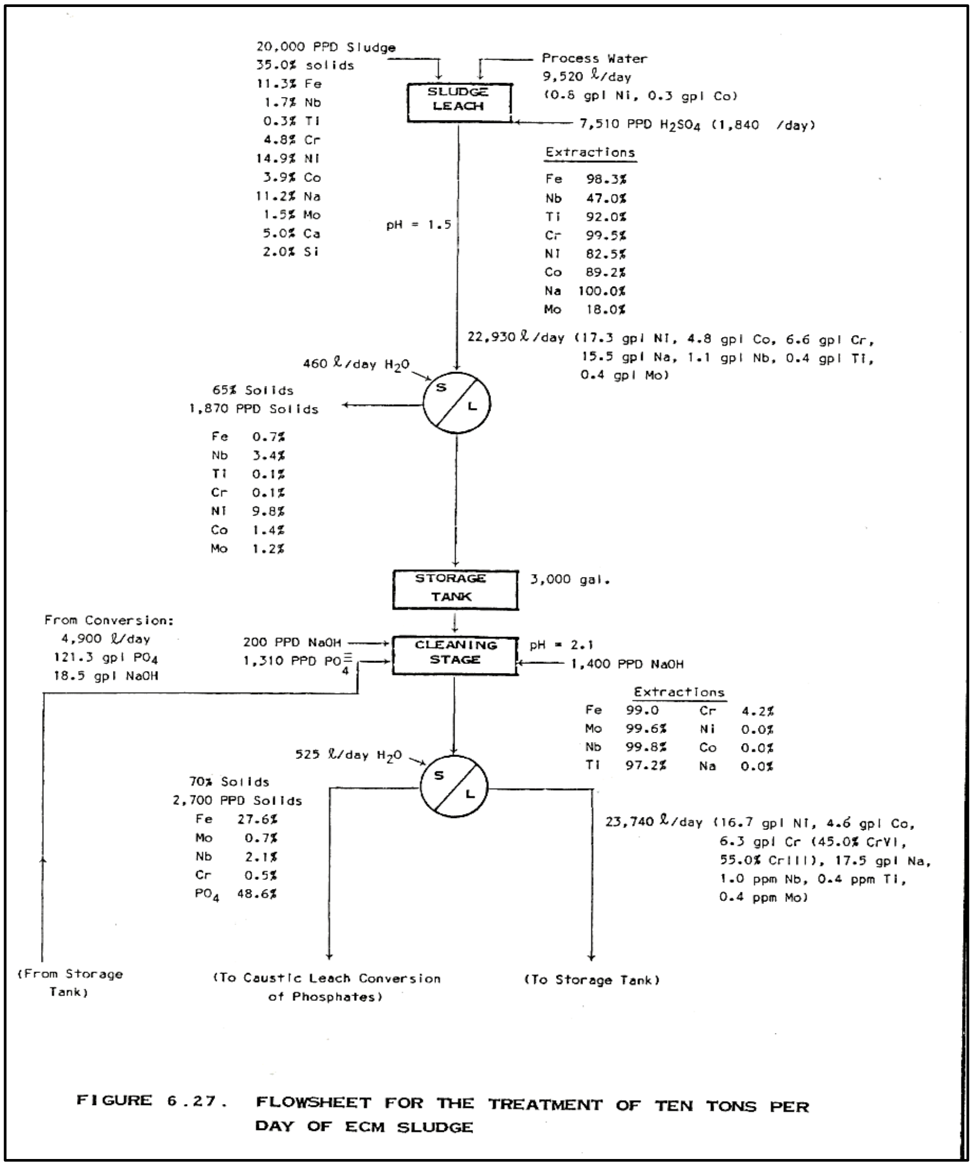


FIGURE 6.27. FLOWSHEET FOR THE TREATMENT OF TEN TONS PER DAY OF ECM SLUDGE

Figure 14. Flowsheet for the treatment of ten tons per day of ECM sludge (including mass distributions) [Figure 6.27 in the Twidwell, L.G., D.R. Dahnke Report, December 1987, pages 142 to 145]

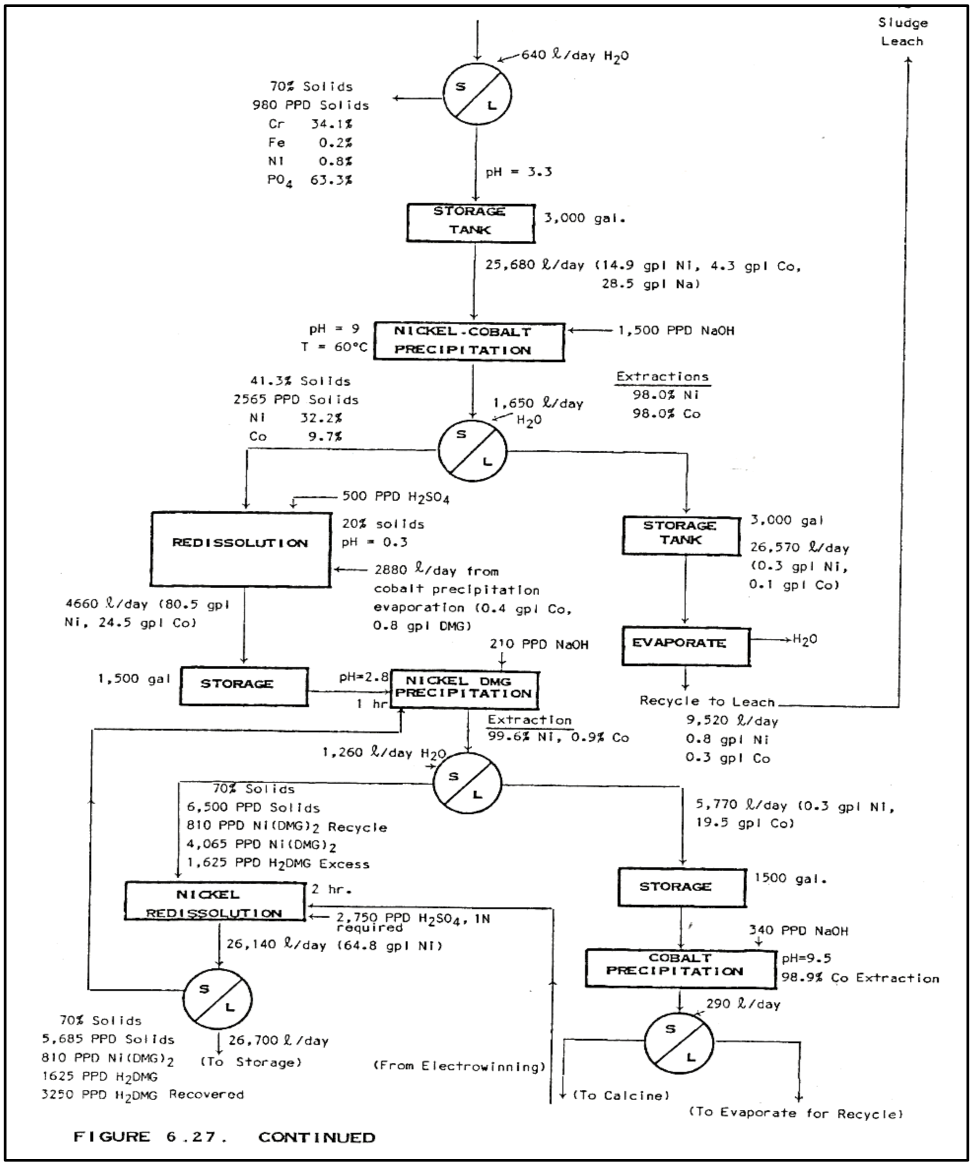


FIGURE 6.27. CONTINUED

Figure 14 (continued). Flowsheet for the treatment of ten tons per day of ECM sludge (including mass distributions) **[Figure 6.27 in the Twidwell, L.G., D.R. Dahnke Report, December 1987, pages 142 to 145]**

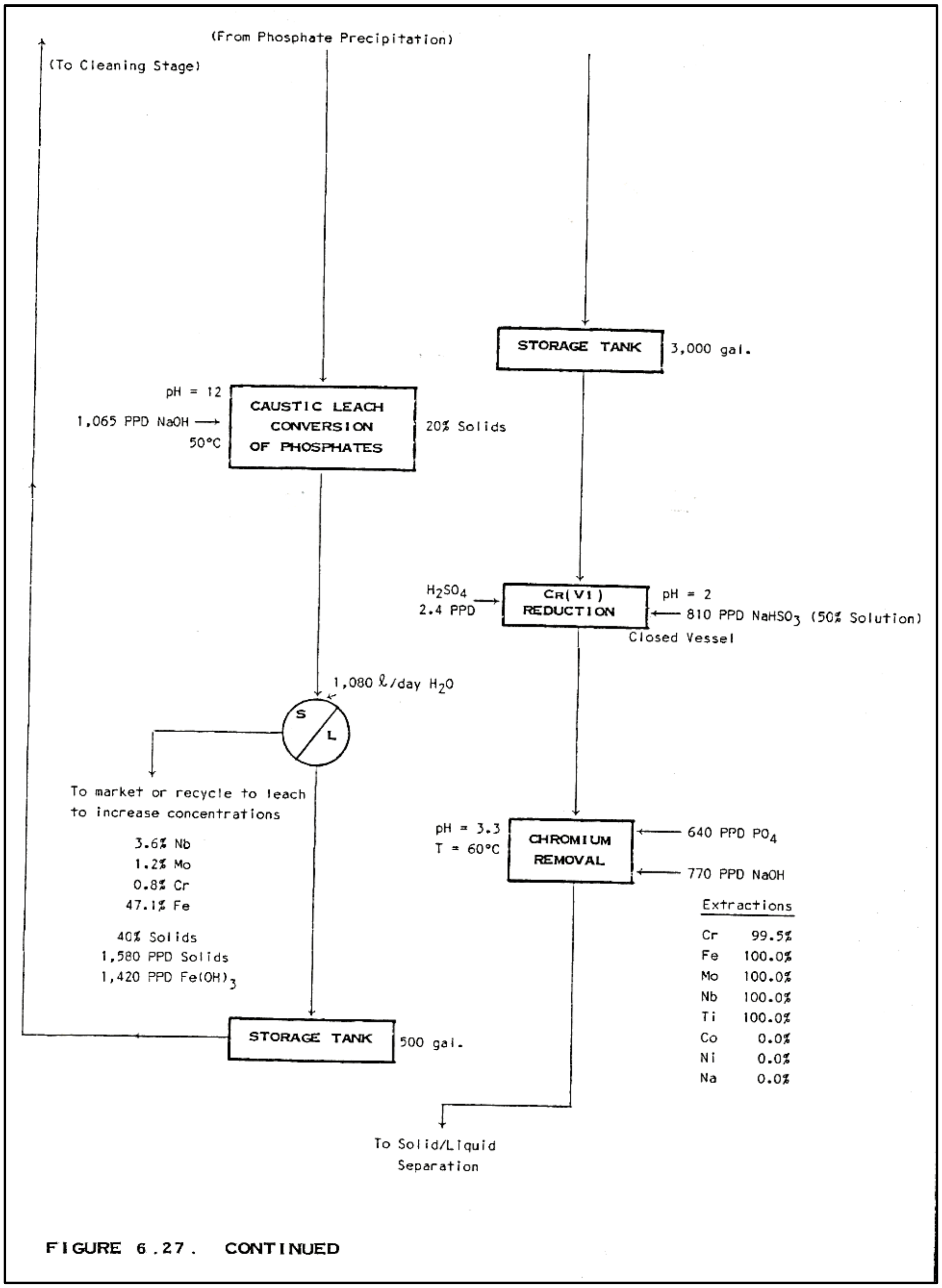


Figure 14 (continued). Flowsheet for the treatment of ten tons per day of ECM sludge (including mass distributions) [Figure 6.27 in the Twidwell, L.G., D.R. Dahnke Report, December 1987, pages 142 to 145]

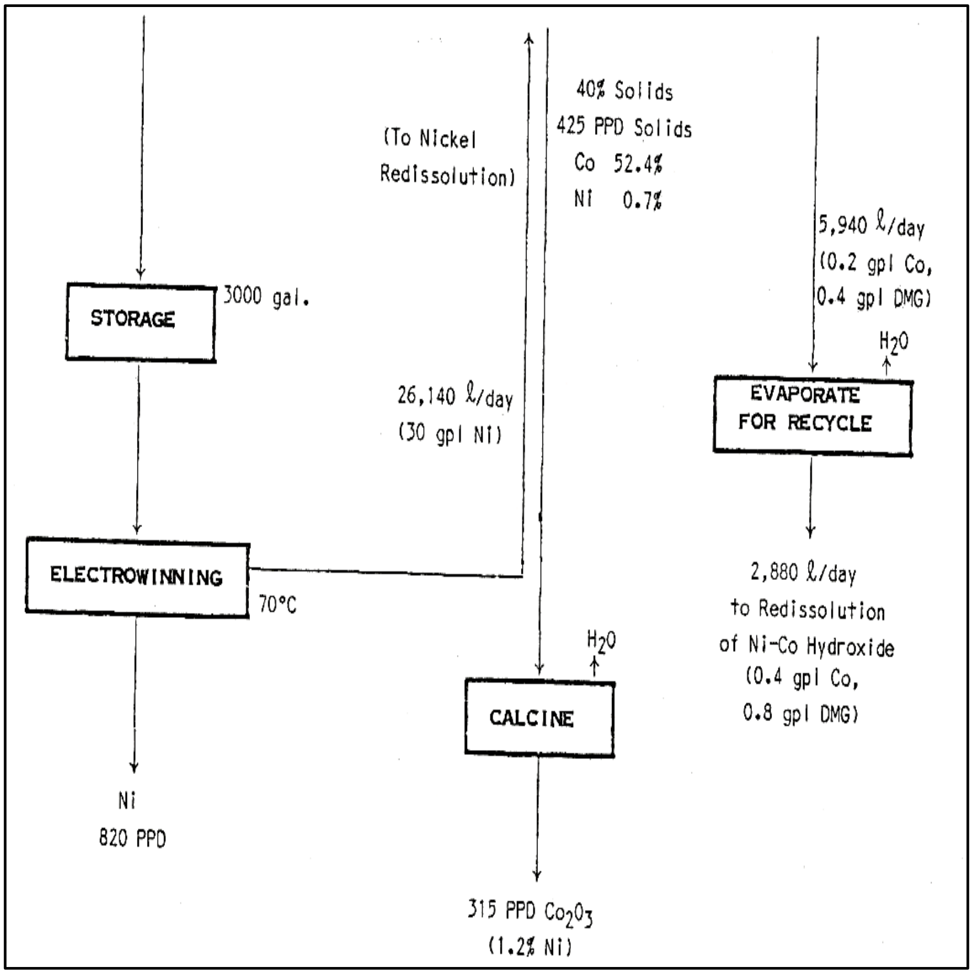


Figure 14 (continued). Flowsheet for the treatment of ten tons per day of ECM sludge (including mass distributions) [Figure 6.27 in the Twidwell, L.G., D.R. Dahnke Report, December 1987, pages 142 to 145]

4. Twidwell, L.G., D.R. Dahnke, Report, December 1987. *Metal Value Recovery from Alloy Chemical Milling Waste: Phase II.*

Abstract

The purpose of the present study was to investigate disposal treatment processes which enable the economic recovery of valuable components, such as cobalt, nickel, and chromium, from hazardous electromachining waste hydroxide sludges. The objectives of the investigation include the collection of experimental data to design a pilot plant (Phase III) to demonstrate the feasibility of the proposed process: the collection of an additional electromachining sludge to verify applicability of proposed flowsheets; the examination of the chromium phosphate conversion unit operation to consider producing products more valuable that chromium phosphate, the investigation of product markets and extent of markets for the anticipated salt products; the identification of equipment appropriate to the flowsheet unit operations, and an engineering cost analysis to determine the economic benefits of adopting commercialization of the treatment of electrochemical machining sludge materials.

These objectives have been accomplished. Flowsheets that have been developed and the data supporting the success of the treatment sequence to selectively separate individual metal values are presented in the following report that demonstrates the applicability of the phosphate-dimethylglyoxime process for

disposing of iron and recovering chromium, nickel, and cobalt from electrochemical machining hydroxide sludge materials. Data are presented summarizing laboratory scale test work; locked cycle test work to determine the effect of recycling solutions and reagents on product purity and loss of reagent materials; and large-scale test work to demonstrate the feasibility of treating significant quantities of the sludge material.

Data are also presented to show that the proposed phosphate process is applicable to several sludge materials, i.e., low and high cobalt containing electrochemical machining sludge materials. The distribution of all major elements through the process products are delineated. Also, the results of an investigation to study the possible conversion of chromium phosphate to more marketable products show that other more useable products can be formed, e.g., sodium chromate or chromic acid.

The products from the proposed flowsheet are all either metal products or common chemical salts, e.g., chromic acid or sodium chromate, metallic nickel or nickel sulfate, metallic cobalt of cobaltic oxide. The markets for these products are well developed and marketability is assured.

The proposed flowsheets require simple, readily available equipment, such as stirred reactors, thickeners, and filer devises. These items are commercially available and new technology need not be developed.

An economic evaluation has been performed for a ten ton per day treatment facility which show that an excellent return o investment (ROI) is possible, e.g., 98+/-29% based on recovered metal and metal salt values and 120+/-35% if a credit is taken for disposal costs (1987 values). This report covers the period October 1,1986 through December 31, 1987.

Brief Conclusions

The conclusions for the Laboratory Test Program are too voluminous to include here. Please refer to Report Section 6.2 Large Scale Test Program; 6.2.1 Iron-Chromium-Nickel (pages 128 to 134) and Section 6.2.2. Iron-Chromium-Nickel-Cobalt (pages 134 to 137)

An example flowsheet is presented in Figure 15 [Figure 6.25 in the **Twidwell, L.G., D.R. Dahnke, Report, December 1987,** page 127 along with data in Tables 6.11 and 6.12.

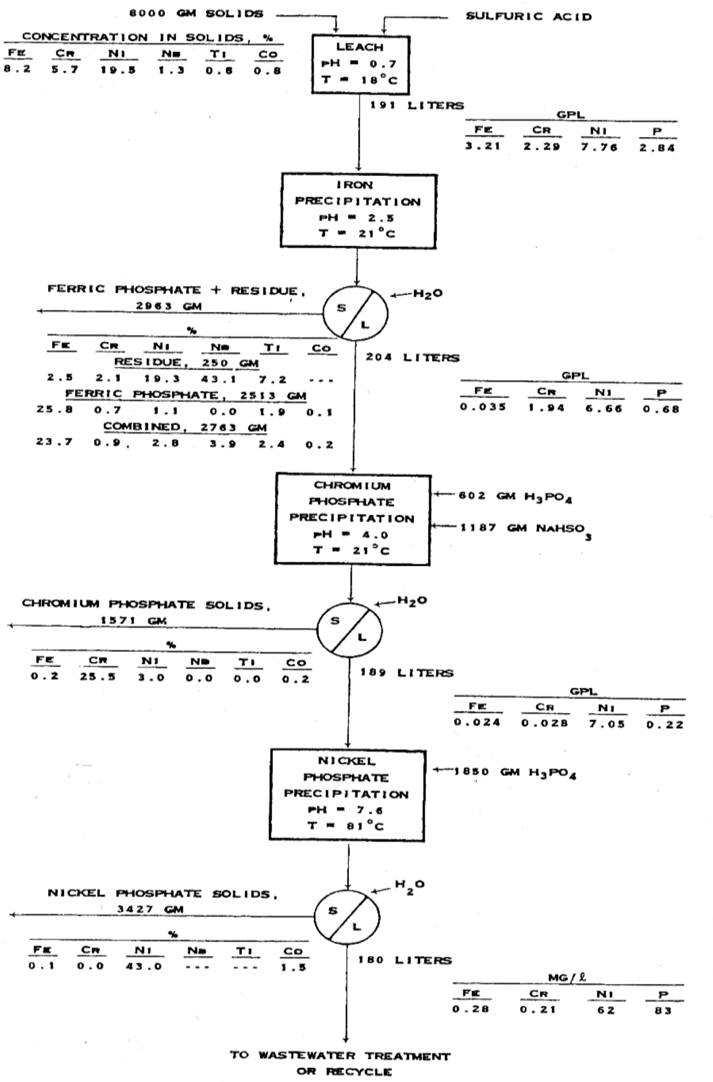


FIGURE 6.25. FLOWSHEET FOR THE SEPARATION OF FE-CR-NI BY PHOSPHATE PRECIPITATION

Figure 15. Flowsheet for the separation of Fe, Cr, Ni by phosphate precipitation [Figure 6.25 in the Twidwell, L.G., D.R. Dahnke Report, December 1987, page 129]

Table 7. EP toxicity test [Table 6.12 in the Twidwell, L.G and D.R. Dahnke Report, July 1987, Page 127]

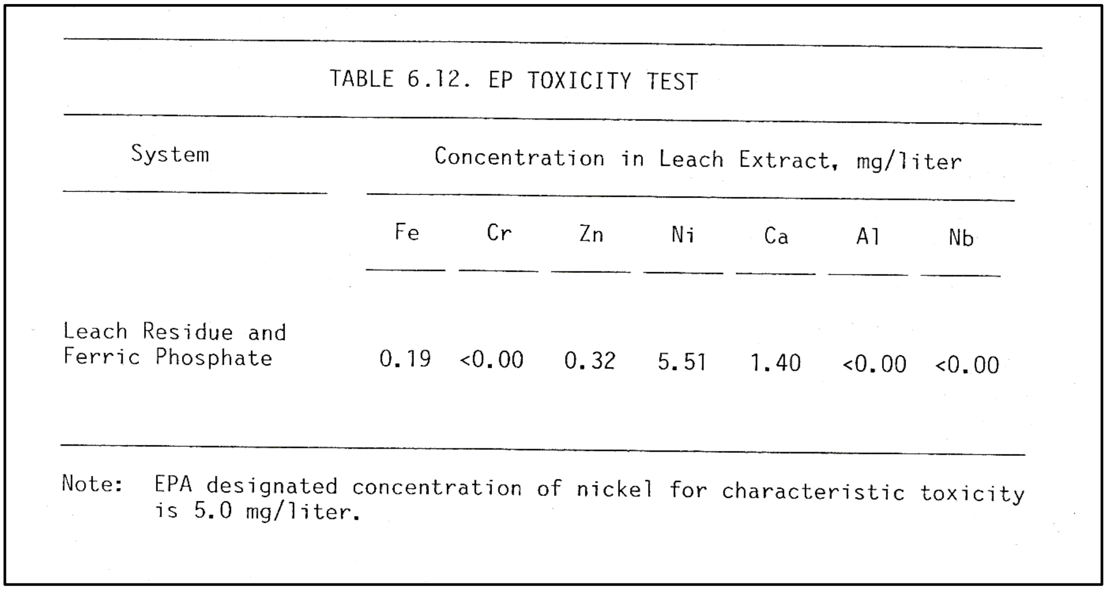


TABLE 6.12. EP TOXICITY TEST

System	Concentration in Leach Extract, mg/liter						
	Fe	Cr	Zn	Ni	Ca	Al	Nb
Leach Residue and Ferric Phosphate	0.19	<0.00	0.32	5.51	1.40	<0.00	<0.00

Note: EPA designated concentration of nickel for characteristic toxicity is 5.0 mg/liter.

Table 8. Element distribution resulting from treatment of Fe-Cr-Ni sludge [Table 6.13 in the Twidwell, L.G., D.R. Dahnke Report, July 1987, Page 128]

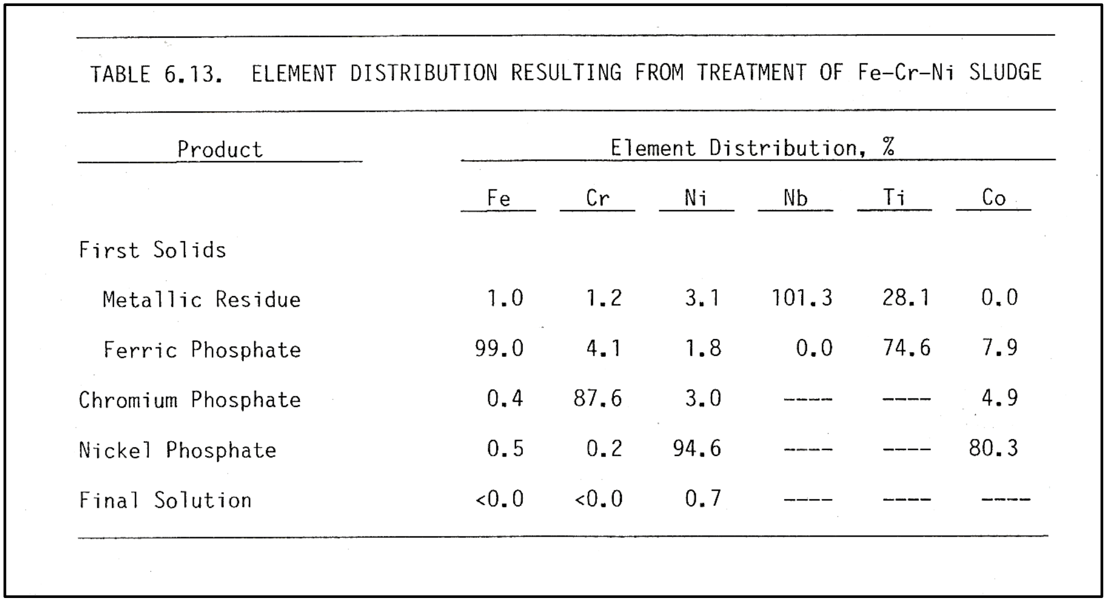


TABLE 6.13. ELEMENT DISTRIBUTION RESULTING FROM TREATMENT OF Fe-Cr-Ni SLUDGE

Product	Element Distribution, %					
	Fe	Cr	Ni	Nb	Ti	Co
First Solids						
Metallic Residue	1.0	1.2	3.1	101.3	28.1	0.0
Ferric Phosphate	99.0	4.1	1.8	0.0	74.6	7.9
Chromium Phosphate	0.4	87.6	3.0	----	----	4.9
Nickel Phosphate	0.5	0.2	94.6	----	----	80.3
Final Solution	<0.0	<0.0	0.7	----	----	----

5. Twidwell, L.G., S.A. Shuey, D.R. Flynn, D.R. Dahnke Publication, 1993. *Selective Recovery of Nickel and Cobalt from Electromachining Sludge Materials,* J. Haz. Waste and Haz. Mat., Vol. 10, No. 4, pp 297-231.

Abstract (Referenced publication 1993)

The recovery of nickel and cobalt from electromachining sludge in the form of relatively high-purity marketable products has been investigated. The investigation has shown that a series of hydrometallurgical unit operations can be performed to recover nickel and cobalt from electromachining sludge in the form of nickelic hydroxide and cobalt sulfate/cobalt metal, respectively. The recovery unit operations for nickel include high pH cyanide complexation, followed by oxidation and precipitation of

nickelic hydroxide. The resultant filtrate can be treated for cobalt concentration and recovery by precipitation of a cobaltous/cobaltic double cyanide salt and cobaltous hydroxide. This concentrated form of cobalt can then be converted to cobalt sulfate by acid baking; then redissolved and electrowon as high purity cobalt metal. Product purity rivals that of conventional multistage solvent extraction processes. First order cost estimation indicates the possibility of excellent return on investment.

Abstract (Shuey Thesis 1993)

The recovery of nickel and cobalt from electromachining sludge in the form of relatively high-purity marketable products has been investigated. The investigation has shown that a series of hydrometallurgical unit operations can be performed to recover nickel and cobalt from electromachining sludge in the form of nickelic hydroxide and cobalt sulfate/cobalt metal, respectively. The recovery unit operations for nickel include high pH cyanide complexation, followed by oxidation and precipitation of nickelic hydroxide. The resultant filtrate can be treated for cobalt concentration and recovery by precipitation of a cobaltous/cobaltic double cyanide salt ($Co^{+2}{}_3[Co^{+3}(CN_6]_2xH_2O$). This concentrated form of cobalt can then be converted to cobalt sulfate by acid baking; then redissolved and electrowon as high purity cobalt metal. Product purity rivals that of conventional multistage solvent extraction processes. First order cost estimation indicates the possibility of excellent return on investment.

Brief Conclusions

Section 3.5.10. Full Scale Test [Twidwell, L.G., S.A. Shuey, D.R. Flynn, D.R. Dahnke. 1993]

All previous tests dealing with metal-cyanide salt precipitation used synthetic solutions. To determine the effectiveness of this process on authentic ECM process solutions, a large-scale test was conducted. An authentic solution was generated by leaching ECM sludge from the Lehr Corp. of Cincinnati, OH.

The Lehr sludge was treated by the previously described Phosphate Process to produce the nickel/cobalt intermediate sludge that was used in developing the nickel/cobalt separation process. The generalized flowsheet is depicted in Figure 17 (Figure 1 in the referenced publication, p301). Elemental distributions to the various products are illustrated in Table 10 (Table 2 in the noted publication, p302). Typical nickel/cobalt residues produced by the Phosphate Process are presented in Table 11 (Table 3 in the noted publication, p302).

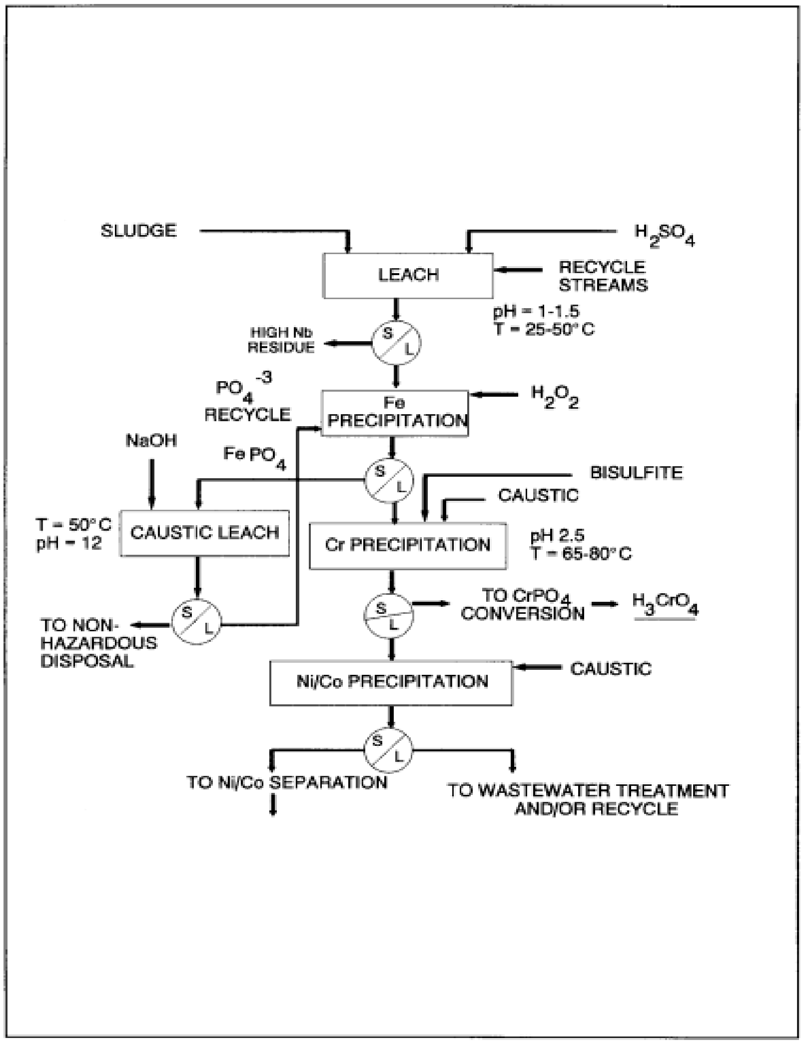


FIGURE 1. Flowsheet for the Treatment of Electrochemical Machining Sludge Materials by the Phosphate Process for Removal of Iron and Recovery of Chromium

Figure 16. Flowsheet for the separation of Fe, Cr, Ni, Co by phosphate precipitation [Figure 1 in the Twidwell, L.G., S.A. Shuey, D.R. Flynn, D.R. Dahnke Publication, 1993, page 301].

Table 9. Typical As-received ECM sludge material [Table 1 in the Twidwell, L.G., S.A. Shuey, D.R. Flynn, D.R. Dahnke. Publication 1993, page 300]

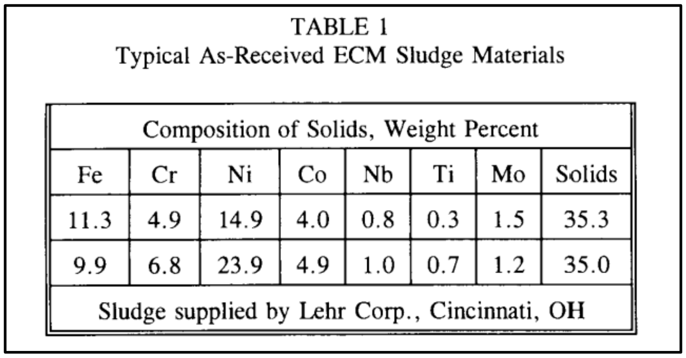


TABLE 1
Typical As-Received ECM Sludge Materials

Composition of Solids, Weight Percent							
Fe	Cr	Ni	Co	Nb	Ti	Mo	Solids
11.3	4.9	14.9	4.0	0.8	0.3	1.5	35.3
9.9	6.8	23.9	4.9	1.0	0.7	1.2	35.0
Sludge supplied by Lehr Corp., Cincinnati, OH							

Table 10. Phosphate process distribution of elements into products (Table 2 in the Twidwell, L.G., S.A. Shuey, D.R. Flynn, D.R. Dahnke Publication, 1993 page 302]

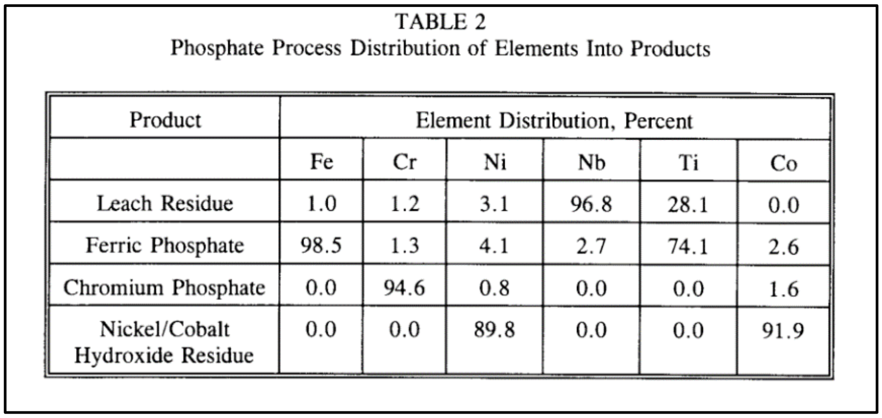


TABLE 2
Phosphate Process Distribution of Elements Into Products

Product	Element Distribution, Percent					
	Fe	Cr	Ni	Nb	Ti	Co
Leach Residue	1.0	1.2	3.1	96.8	28.1	0.0
Ferric Phosphate	98.5	1.3	4.1	2.7	74.1	2.6
Chromium Phosphate	0.0	94.6	0.8	0.0	0.0	1.6
Nickel/Cobalt Hydroxide Residue	0.0	0.0	89.8	0.0	0.0	91.9

Table 11. Nickel/Cobalt residues from the phosphate process (Table 3 in the Twidwell, L.G., S.A. Shuey, D.R. Flynn, D.R. Dahnke Publication, 1993, page 302]

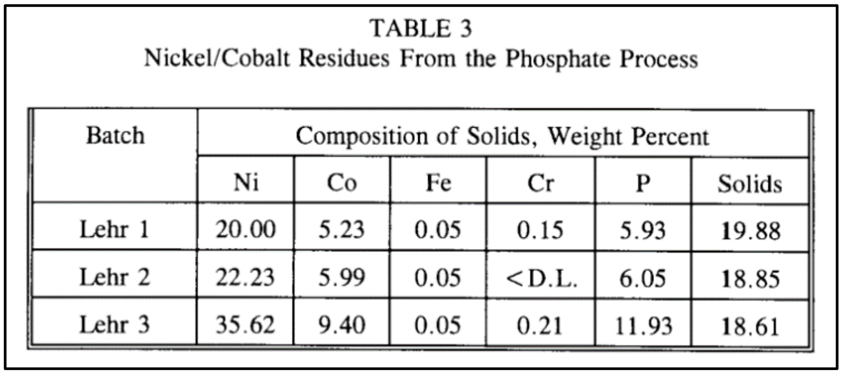


TABLE 3
Nickel/Cobalt Residues From the Phosphate Process

Batch	Composition of Solids, Weight Percent					
	Ni	Co	Fe	Cr	P	Solids
Lehr 1	20.00	5.23	0.05	0.15	5.93	19.88
Lehr 2	22.23	5.99	0.05	<D.L.	6.05	18.85
Lehr 3	35.62	9.40	0.05	0.21	11.93	18.61

Cyanide Process

The first stage of the process is leaching the sludge with sulfuric acid at a pH from 1-1.5, leaving a residue consisting primarily of silica, but may contain a relatively high concentration of niobium. Phosphate chemistry is then used to remove trivalent cations from divalent cations. Ferrous iron in solution is oxidized with the addition of hydrogen peroxide and precipitated as ferric phosphate with the addition of phosphoric acid at a pH = 1.5-2.0 at ambient temperature. The phosphate is reclaimed by converting the ferric phosphate to ferric hydroxide using a caustic leach. Other metals, such as titanium and molybdenum are removed with the iron (The residue resulting from this conversion is non-hazardous and can be disposed of in an industrial landfill). Next, hexavalent chromium is reduced to trivalent chromium with the addition of sodium bisulfite and precipitated as chromium phosphate at a pH = 2.5 and a temperature of 65-80°C. The chromium phosphate may then be converted to chromic acid, a salable product. The primary metals remaining in solution, cobalt and nickel, are then precipitated by pH control and sent on to further processing. The production of a high purity chromic acid and the possibility of high purity cobalt and nickel products and the recovery of niobium make this application of the phosphate process economically feasible.

A nickel/cobalt separation process shows excellent promise for recovery of high purity cobalt and nickel products, i.e., redissolution of the nickel/cobalt hydroxide solids in a cyanide solution with subsequent recovery of high purity nickel by oxidative precipitation of nickelic hydroxide. The cobalt is subsequently (after removal of the nickelic hydroxide) recovered from solution. The production of the nickel/cobalt hydroxide material was illustrated in Figure 16. The subsequent treatment of the hydroxide material is presented in Figure 17. The nickel/cobalt hydroxide residue is dissolved and complexed in an alkaline (pH > 14) sodium or potassium cyanide solution. The nickel/cobalt cyanide solution is then oxidized with sodium hypochlorite, producing a nickelic hydroxide solid and a stable aqueous cobaltic cyanide bearing solution. This cobaltic cyanide solution is evaporated, producing a concentrate, which is then acid baked with sulfuric acid at elevated temperatures. The resulting cobaltous sulfate is then redissolved and electrowon. Cyanide destruction during the baking process has been shown to be complete and non-hazardous. The nickel/cobalt ratio in the nickelic hydroxide product is > 600 and the Co/Ni ratio in the cobaltous cyanide solution is > 1500 (see Table 12) . **Shuey (1990)** investigated methods for cobalt recovery from the nickel depleted solutions. The most successful approach was to concentrate the cobalt by precipitation of double cobalt cyanide solids (see Figures 18 to 20).

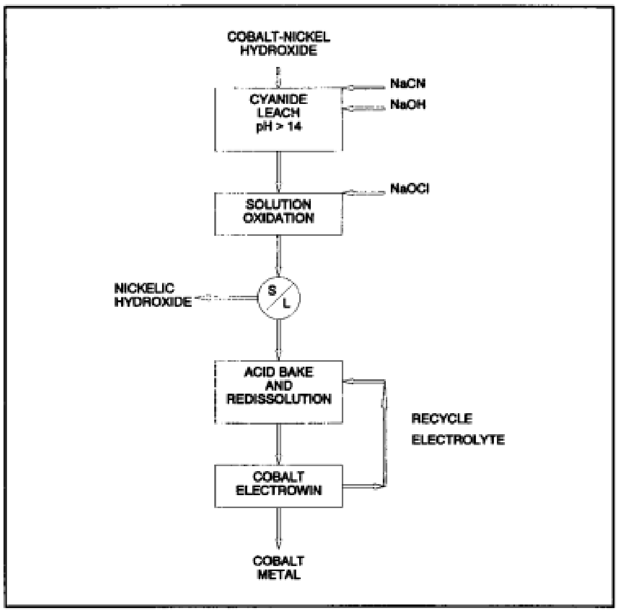


FIGURE 2. Flowsheet for the Treatment of Nickel/Cobalt Residues by Dissolution in Cyanide with Subsequent Selective Recovery of High Purity Nickel and Cobalt

Figure 17. Flowsheet for the treatment of Nickel/Cobalt residues by dissolution in Cyanide with subsequent selective recovery of high purity Nickel and Cobalt [Figure 2 in the Twidwell, L.G., S.A. Shuey, D.R. Flynn, D.R. Dahnke Publication, 1993, page 303]

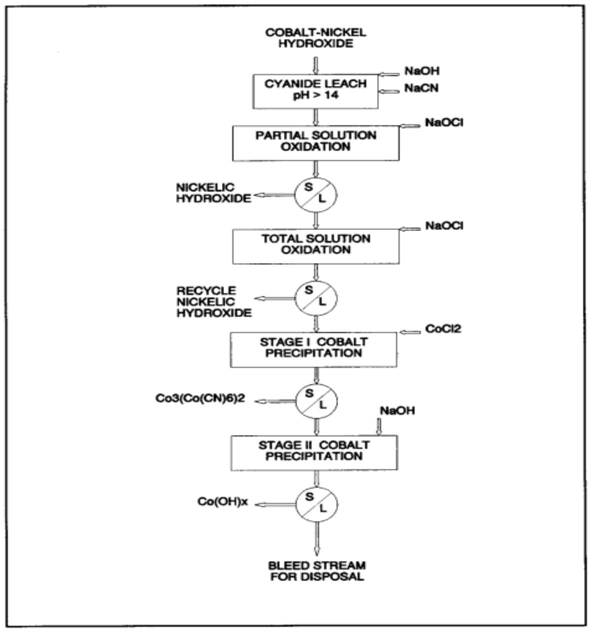


FIGURE 3 Flowsheet for the Shuey Process for Selectively Separating Nickel from Cobalt

Figure 18. Flowsheet for the Shuey Process for selectively separating Nickel from Cobalt [Figure 3 in the Twidwell, L.G., S.A. Shuey, D.R. Flynn, D.R. Dahnke Publication, 1993, page 305]

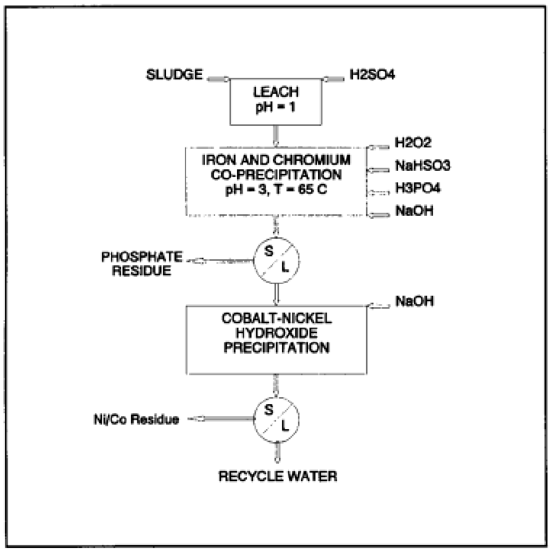


FIGURE 4. Flowsheet for Large Scale Test Performed on Lehr Sludge to Produce the Nickel/Cobalt Residue Required for Demonstration of Selective Separation of Nickel and Cobalt

Figure 19. Flowsheet for the Large Scale test performed on Lehr Sludge to produce the Nickel/Cobalt residue required for demonstration of selective separation of Nickel and Cobalt [Figure 4 in the Twidwell, L.G., S.A. Shuey, D.R. Flynn, D.R. Dahnke Publication, 1993, page 306]

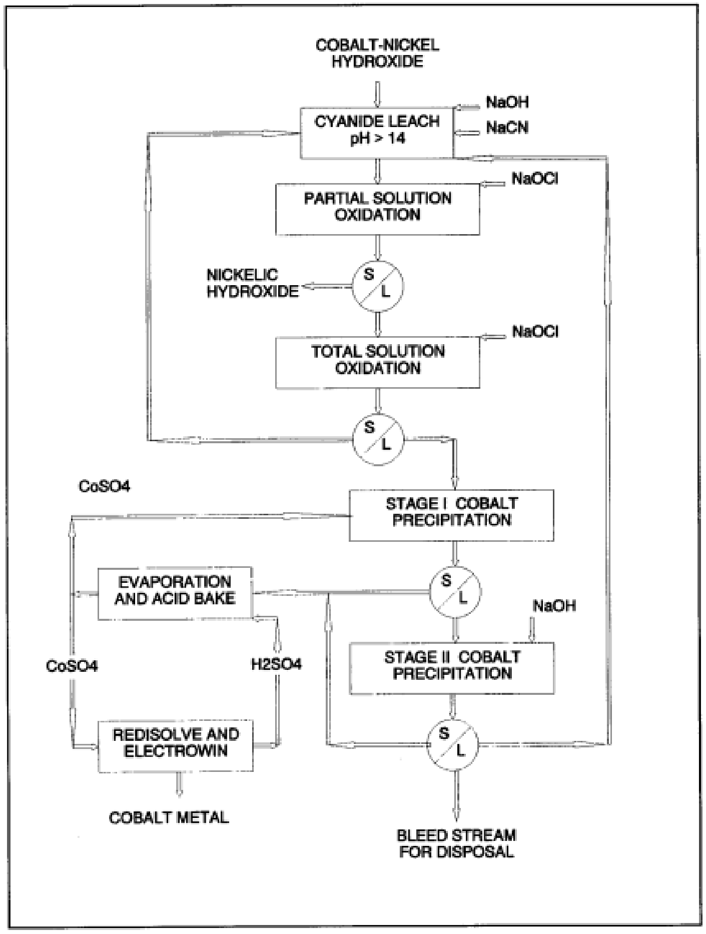


FIGURE 5. Flowsheet for Treatment of Nickel/Cobalt Hydroxide Residues by Cyanide Leaching, Nickelic Precipitation by Oxidation and Cobalt Recovery by Double Salt Precipitation

Figure 20. Flowsheet for treatment of Nickel/Cobalt hydroxide residues by Cyanide leaching. Nickelic precipitation by oxidation and Cobalt recovery by Double Salt precipitation. [Figure 5 in the Twidwell, L.G., S.A. Shuey, D.R. Flynn, D.R. Dahnke Publication. 1993, page 307]

Table 12. Nickel/Cobalt product purity (Table 7 in the Twidwell, L.G., S.A. Shuey, D.R. Flynn, D.R. Dahnke Publication, 1993 page 302]

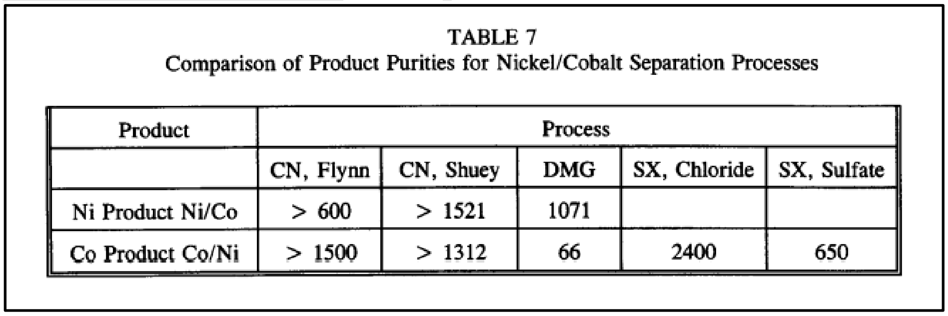


TABLE 7
Comparison of Product Purities for Nickel/Cobalt Separation Processes

Product	Process				
	CN, Flynn	CN, Shuey	DMG	SX, Chloride	SX, Sulfate
Ni Product Ni/Co	> 600	> 1521	1071		
Co Product Co/Ni	> 1500	> 1312	66	2400	650

6. Twidwell, L.G., S.F McGrath Report. ***Treatability Study for Encycle/Texas Metal Recovery from Hydroxide Sludge Materials.*** **1988.**

Study Objectives

The goal of the study was to develop an appropriate flowsheet for the treatment of specific metal hydroxide sludge material containing copper, chromium, iron, cadmium, zinc, and nickel. Previous studies (on bench and pilot scale) demonstrated that selective and effective metal value separations were possible.

The flowsheet investigated included the following sequential unit operations: sludge leach, copper cementation on iron, chromium phosphate precipitation, chromium phosphate conversion, iron oxidation and ferric phosphate precipitation, cadmium cementation on zinc, and zinc solvent extraction. A great deal of the process information developed in previous studied for the treatment of multicomponent leach solutions was applied in this study.

Brief Conclusions

The proposed Encycle/Texas flowsheet has been shown to be appropriate for metal value recovery excerpt for the noted problems dealing with cadmium. Copper can be effectively removed by cementation with iron, chromium can be selectively removed from solution by phosphate precipitation, chromium phosphate can be converted to chromic acid by nitrate fusion, iron can be selectively removed from solution by oxidation and precipitation of ferric phosphate, and zinc can be recovered by solvent extraction. Refer to Section 2.4.3 of the referenced report for a summary of the conclusions for each unit operation when 750 grams of sludge was treated sequentially (see pages 12 to 14 and 65 to 68).

STUDIES PERFORMED BY M.Sc. RESEARCHERS

(During the Development of the Sequential Treatment of Metal Hydroxide Sludge-Abstracts are Included)

Laney, D. 1984. *The Application of Solvent Extraction to Complex Metal Bearing Solutions,* **M.Sc. Thesis,** Department of Metallurgical/Mineral Processing Engineering, Montana College of Mineral Science and Technology (Now Montana Technological University) Butte, MT. 140p.

Abstract

The objectives of this research were to investigate: 1. The application of existing solvent extraction techniques and reagents to complex metal bearing solutions; specifically solutions containing copper, iron, zinc, nickel, chromium, aluminum and calcium were investigated. 2. Separation and recovery of metal values in such a way as to be amenable to continuous plant operations. This study demonstrated that: Copper could be selectively removed from a mixed metal solution containing copper, zinc, nickel, and chromium by solvent extraction using LIX 622, Zinc could be selectively removed from a mixed metal solution containing iron, nickel and chromium by solvent extraction using D2EHPA, and Iron (in concentrations < 1 gpl) could be extracted along with zinc from a mixed metal solution by D2EHPA and subsequently selectively rejected from the organic phase by hydrochloric acid stripping. Data are presented and discussed summarizing the results of small-scale batch shake test work, small-scale continuous test work (600cc cells) and large-scale continuous test work (four-liter cells).

Dahlke, D. 1985. *Removal of Iron from Process Solutions,* **M.Sc. Thesis,** Department of Metallurgical/Mineral Processing Engineering, Montana College of Mineral Science and Technology (Now Montana Technological University) Butte, MT. 361p.

Abstract

An investigation into three methods for selectively removing iron from acidic, mixed-metal, aqueous solutions has been conducted. Two of these methods, i.e., jarosite precipitation and solvent extraction, were adaptations of commercially implemented processes. The third process, ferric phosphate precipitation, was inadvertently discovered to be an effective and selective technique for extracting iron from acidic, aqueous solutions, and preliminary tests have been performed. Jarosite precipitation was applied to high-iron bearing, mixed-metal solutions, and proved to be a viable process with two circumstantial exceptions: chromium, if present in valuable concentrations in the aqueous solution, will precipitate in prohibitive quantities with the jarosite; and secondly, jarosite is not applicable to low-iron bearing solutions because of poor filtering characteristics of the precipitated solid. Solvent extraction of iron was developed primarily to treat low iron bearing solutions. Coextraction of iron and zinc with DEHPA followed by selective stripping to separate these metals was shown to be an adequate technique for removing these two metals from aqueous solutions. Stripping of iron in this process, however, was not refined sufficiently to suggest commercial application of this process, and the success of solvent extraction in this application is likely dependent upon the development of an economically feasible method for stripping iron. Precipitation of trivalent-metal, phosphate compounds was demonstrated to be an effective and selective method for removing species from solutions which also contain various divalent cation species.

Arthur, B. 1987. *Treatment of Iron, Chromium, and Nickel Aqueous Chloride Acidic Solutions by Phosphate Precipitation,* **M.Sc. Thesis,** Department of Metallurgical/Mineral Processing Engineering, Montana College of Mineral Science and Technology (Now Montana Technological University) Butte, MT. 129p.

Abstract

Flowsheets to separate iron, chromium, and nickel from stainless steel pickle liquor and superalloy scrap leach solutions by phosphate precipitation have been investigated. Flowsheet development was performed on laboratory-prepared stock solutions. The results from prepared solutions were then applied to superalloy electrochemical machining sludge leach solutions. Phosphate precipitation produced very encouraging results for selective separation of iron and recovery of chromium and nickel. The present research has emphasized the development of techniques for the removal of iron and the recovery of chromium and nickel by phosphate precipitation from chloride and sulfate bearing solutions. Experimental data are presented and discussed to support several proposed flowsheets applicable to present industrial waste materials.

Konda, E. 1986. *Study of Ferric Phosphate Precipitation as a means of Iron removal from Zinc-bearing Acidic Aqueous Solutions,* **M.Sc. Thesis,** Department of Metallurgical/Mineral Processing Engineering, Montana College of Mineral Science and Technology (Now Montana Technological University) Butte, MT. 314p.

Abstract

The method of selectively removing iron from mixed-metal acidic solutions as ferric phosphate, discovered in 1985 by Dahnke(l), has been extensively studied. Phosphate precipitation has been shown to have the potential to replace current aqueous iron removal techniques, and experimental variables necessary for industrial applications have been studied. Ferric phosphate precipitation was found to be selective for iron, and a flowsheet for iron removal from zinc has been proven to be exceptionally simple as compared to that of current industrial technology. Energy and residence time requirements for removing iron from solution have been demonstrated to be at least half that required for industrial iron-zinc processes. Ferric phosphate may be marketable as a product. Processes in which an inherent objective is to remove and dispose of iron can be retrofitted with the ferric phosphate flowsheet, and if

desired, ferric phosphate can be converted to ferric hydroxide; thus affording phosphate recycling and production of a stable ferric hydroxide waste. Relevant chemistry and thermodynamic data were developed at standard and elevated temperatures for the formation of phosphate compounds. Metal species were precipitated as phosphates from sulfate solutions containing iron, nickel, zinc, and chromium. From acquired data, phosphate stability diagrams were constructed. Phosphate precipitate free energies of formation were also derived.

Downey, J. 1982. *A Study of Mixed Solvent Extraction Reagents Potentially Useful for Treatment of Aqueous Solutions Containing Nickel,* **M.Sc. Thesis,** Department of Metallurgical/Mineral Processing Engineering, Montana College of Mineral Science and Technology (Now Montana Technological University) Butte, MT. 101p.

Abstract
The selective recovery of nickel from aqueous mixed metal solutions was the desired goal of this research. Only solvent extraction techniques were considered experimentally, but other potential approaches are discussed. Emphasis was placed on nickel and chromium (III) solutions. Two mixed organic extractants were considered, i.e., an EHO (2-ethyl hexanal oxime) - D2EHPA (Di ethyl hexyl phosphoric acid), and a L1X63- D2EHPA system. The EHO system was not pursued beyond small scale shake tests because the reagent is not commercially available. The LIX63 system was studied in a continuous solvent extraction test rack. The results of this study show that the LIX63 – D2EHPA mixture deteriorates rapidly in the mixed extractant system during the stripping operation. Experimental results are presented and discussed.

Nordwick, S. 1987. *Conversion of Precipitated Ferric Phosphate to Ferric Hydroxide,* **M.Sc. Thesis,** Department of Metallurgical/Mineral Processing Engineering, Montana College of Mineral Science and Technology (Now Montana Technological University) Butte, MT. 101p.

Abstract
The conversion of ferric phosphate dihydrate to ferric hydroxide has been investigated. A series of kinetic studies have been performed to evaluate the rate of the conversion reaction: FeP04'2H20(s) + H20 ---> Fe(0H)3($) + HP04 = + 2H+. The rate of the reaction was followed by exposing a slurry of ferric phosphate to a water environment, the pH of which was controlled with NaOH, and by measuring the concentration of phosphate in solution as function of time. Thermodynamically, ferric phosphate should convert to ferric hydroxide at a pH of approximately three at 25°C. However, it was found that for good conversion (85.6 %) a pH of 11 was required at 80°C. The best conversion (94.8 %) was obtained at a pH of 12 and 50°C. For the first part of the reaction, the rate follows the product layer shrinking core model and is controlled by either the diffusion of hydroxide or phosphate through the product layer.

Rapkoch, J. M. 1987. *The Effects on Metal Phosphate Precipitation from Complex Solutions by Substituting Sodium Hydroxide, the Titrant, with Ammonium Hydroxide,* **M.Sc. Thesis,** Department of Metallurgical/Mineral Processing Engineering, Montana College of Mineral Science and Technology (Now Montana Technological University) Butte, MT. 152p.

Abstract
Metal removal from complex metal bearing solutions by phosphate precipitation was investigated using ammonium hydroxide and ammonia gas as neutralizing agents. The main focus of the research was to determine if these reagents were effective substitutes for sodium hydroxide. Additionally, the investigation considered whether soluble transition-metal ammine complexes would inhibit the formation of insoluble phosphates in sequential metal precipitation schemes and in systems with variable concentrations of ammonium ions. The experiments were carried out using standard methods of separation and analysis used in previous research on metal phosphate precipitation from sludge-oriented

solutions, and solubility data generated during the experiments were used to interpret the results. Two new phases of nickel ammonium phosphate were formed; the new compounds identified are NH4NiP04:4H20 and NH4NiPO4:0.67H2O. Their unique x-ray diffraction data were submitted to the JCPDS for publication and will appear in the next set of x-ray data file cards. The free energy of formation for the room temperature nickel ammonium phosphate was derived with the aid of computer programs. The value for NH4NiP04:4H20 is -520.0 +1.0 kcal/mole. This information was then used to generate a stability diagram for the nickel(II) - ammonium - phosphate - water system at room temperature.

Flynn, Dale. 1990. *Recovery of Nickel and Cobalt From Electromachining Process Solutions,* **M.Sc. Thesis,** Department of Metallurgical/Mineral Processing Engineering, Montana College of Mineral Science and Technology (Now Montana Technological University) Butte, MT. 162p.

Abstract

The recovery of nickel and cobalt from electromachining sludges in the form of high purity marketable products has been investigated. The investigation has shown that a series of metallurgical unit operations can be performed to recover nickel and cobalt from electromachining sludges in the form of alkali nickelic hydroxide and cobalt sulfate/cobalt metal respectively. The recovery unit operations for nickel include a high pH, cyanide complexation, followed by oxidation and precipitation of the nickel complexes. Subsequent treatment of the resultant filtrate from the precipitation for cobalt recovery is by neutralization of the solution pH and acid baking with concentrated sulfuric acid to produce cobalt sulfate. The cobalt sulfate formed then can be fed into an electrowinning cell to produce pure cobalt metal. Results from laboratory bench scale tests are discussed in terms of appropriate operating conditions for each unit operation in the precipitation and conversion process.

McGrath, Steve. 1992. *The Rate of Precipitation of Chromium Phosphate,* **M.Sc. Thesis,** Department of Metallurgical/Mineral Processing Engineering, Montana College of Mineral Science and Technology (Now Montana Technological University) Butte, MT. 162p.

Abstract

Chromium (III) phosphate precipitation is one of the important unit operations in a process designed to treat metal containing waste materials from the metal finishing industry. Solubility calculations using available thermodynamic data for the system do not correctly predict experimentally observed solubilities. There have been some attempts to recalculate thermodynamic data for aqueous chromium(III) complexes by investigators independently working in the chromium phosphate system and the chromium water system. They disagree with each other and with previously published data for the stability of the dimeric and trimeric chromium hydroxide oligomers.

An independent assessment of the published stability constants of the dimeric and trimeric hydrolytic oligomers at 25°C was attempted in this study giving a value of -log P°c; = 5.01 and -log p°(3i4) = 8.25; both results are very close to published data prior to the estimation from the above solubility measurements, suggesting that kinetic and other factors related to the formation of the respective solids in each system gave inconsistent results when attempts were made to estimate the stability of aqueous species from the solubility measurements.

Additionally, an investigation of the kinetics of chromium phosphate precipitation was made in simulated leach solutions from the process. The apparent Arrhenius energy of activation for precipitation was found to be 33.3±0.9 kcal/mole at pH 3.1. The apparent activation energy for the nucleation and initial growth of the particles was found to be the same. This high activation energy indicates that the process is under chemical control and apparently is related to the rate of exchange of a phosphate ligand with a primary hydration sphere water on chromium atom already incorporated into the surface of the growing particles.

Quinn, J. 1988. *Conversion of Chromium Phosphate to Chromic Acid by Fusion Process,* **M.Sc. Thesis,** Department of Metallurgical/Mineral Processing Engineering, Montana College of Mineral Science and Technology (Now Montana Technological University) Butte, MT. 106p.

Abstract

Conversion of chromium phosphate to more marketable forms has been investigated. The investigation has shown that a series of metallurgical unit operations can be performed to convert chromium phosphate to either solid sodium chromate crystals or a weak strength chromic acid solution. The conversion unit operations include a sodium carbonate fusion followed by a simple fusion product leach. Subsequent treatment of the resultant leach filtrate provides for iron and phosphorous removal through ferric phosphate precipitation. The effluent solution stream is then evaporated to produce sodium chromate crystals or treated for sodium removal by ion exchange to produce chromic acid. Results from laboratory bench scale tests are discussed in terms of optimum operating conditions for each unit operation in the conversion process.

Donelon, D.M. 1989. *Recovery of Metal Values from Spent Stainless Steel Pickle Liquors.* **M.Sc. Thesis,** Department of Metallurgical/Mineral Processing Engineering, Montana College of Mineral Science and Technology (Now Montana Technological University) Butte, MT. 149p.

Abstract

The selective separation of iron, nickel, chromium, and manganese contained in HNO3/HF bearing pickling acids was investigated. This work showed that iron and chromium were selectively removed from solution by precipitating them as their phosphate salts. Manganese was recovered by taking advantage of its oxidation to the +4 state, thus forming insoluble Mn02. Nickel was also oxidized during the recovery of manganese and therefore recovered as NiO(OH). Manganese dioxide and NiO(OH) were directly marketable forms. Iron phosphate was converted to a disposable form of Fe(OH)3, and the aqueous phosphate was then recycled back to the iron removal operation. Chromium phosphate was oxidized by sodium carbonate fusion to produce a marketable chromic acid.

Leary, R. 1990. *Treatment of Stainless Steel Pickling Liquors,* **M.Sc. Thesis,** Department of Metallurgical/Mineral Processing Engineering, Montana College of Mineral Science and Technology (Now Montana Technological University) Butte, MT. 66p.

Abstract

A survey of several techniques for the recovery of Hydrofluoric and Nitric Acid from a spent stainless steel pickle liquor has been performed. The purpose of the study was to determine the feasibility of Ion Exchange, Solvent Extraction, and Diffusion Dialysis as a means to recover HF and HN03. Two different types of Ion Exchange resins were utilized. First, Amberlite IR-120 cation exchange resin was useful for the separation of metals from the complexed anions, however, it did not produce a regenerated acid of sufficient strength to be useful. Second, Amberlite IRA-400 anion exchange resin was able to extract nitric acid sufficiently well, but, fluoride, which was present as a cationic metals complex, was not readily removed from solution. Attempts to break the Ferric Fluoride complex with sulfuric acid had mixed results. The second technique surveyed was Solvent Extraction . The solvent extraction of HF and HN03 by a mixture of 15v/o D2EHPA, 60v/o Tri-butyl phosphate and the balance Kermac 51 OB kerosene proved to be quite successful after addition of sulfuric acid to the raw pickle liquor. Finally, Diffusion Dialysis with an anion selective membrane was the third technique surveyed . Diffusion Dialysis was largely successful only after the metallic fluoride complexes were destroyed by neutralization with KOH. A regenerated acid bath containing 85 gpl HN03 and 10.33 gpl HF could be made by this technique.

Shuey, Scott. 1992. *Survey of Techniques for the Separation of Cobalt and Nickel* (*Selective Separation of Nickel and Cobalt from Electro-machining Sludges),* **M.Sc. Thesis,** Department of

Metallurgical/Mineral Processing Engineering, Montana College of Mineral Science and Technology (Now Montana Technological University) Butte, MT. 68p.

Abstract

The major current process utilized for the separation of high purity cobalt and nickel from a mixed cobalt-nickel chloride or sulphate solution is solvent extraction. This form of metallurgical operation is very capital intensive, because multiple strip and wash stages are required. Studies at Montana Tech have been directed toward development of a treatment process that involves a simple selective precipitation separation. This has resulted in the designing of a cyanide leach/separation process for the separation of cobalt and nickel. A literature review produced a number of articles describing analytical techniques used for the separation of cobalt and nickel. These techniques were reviewed to determine if they could be applied industrially in conjunction with a previous process developed at Montana Tech involving the recovery of metal values from electroplating and electromachining sludge materials. The result of the evaluations were that the analytical techniques could not be adapted to industrial use because of either technical or economical reasons. Attention was then focused on the recovery of cobalt from cyanide process solutions. The present study has shown that a number of hydrometallurgical unit operations can be performed to economically remove cobaltic cyanide from solution for processing into high purity cobalt metal. The precipitation of a complex cobalt-cyanide salt is accomplished with a first stage operation consisting of the addition of a soluble cobaltous salt, that precipitates the complex salt which is then filtered. A second stage operation, consisting of pH adjustment, is then performed. This results in the removal ii of all remaining cobalt from solution. The inclusion of this technology in the previously designed process for the recovery of metal values from electroplating and electromachining sludge materials should result in an economical process to reclaim valuable metals from the waste streams of modem industry, reducing the United States' dependence on foreign sources for a number of strategic metals.

The recovery of nickel and cobalt from electromachining sludge in the form of relatively high-purity marketable products has been investigated. The investigation has shown that a series of hydrometallurgical unit operations can be performed to recover nickel and cobalt from electromachining sludge in the form of nickelic hydroxide and cobalt sulfate/cobalt metal, respectively. The recovery unit operations for nickel include high pH cyanide complexation, followed by oxidation and precipitation of nickelic hydroxide. The resultant filtrate can be treated for cobalt concentration and recovery by precipitation of a cobaltous/cobaltic double cyanide salt and cobaltous hydroxide. This concentrated form of cobalt can then be converted to cobalt sulfate by acid baking; then redissolved and electrowon as high purity cobalt metal. Product purity rivals that of conventional multistage solvent extraction processes. First order cost estimation indicates the possibility of excellent return on investment.

THE TREATMENT SEQUENCE

The following studies were conducted that lead to the development of the sequential treatment of metal hydroxide sludge (both electroplating and electromachining sources)

Author	Year	Master of Science Thesis Titles
Laney, D.	1984	*The Application of Solvent Extraction to Complex Metal Bearing Solutions*
Dahnke, D.	1985	*Removal of Iron from Process Solutions*
Downey, J.	1982	*Separation and Recovery of Chromium and Nickel from Mixed Metal Solutions*
Konda, E.	1986	*Study of Ferric Phosphate Precipitation as a means of Iron removal from Zinc-bearing Acidic Aqueous Solutions*
Nordwick, S.	1987	*Conversion of Precipitated Ferric Phosphate to Ferric Hydroxide*

Author	Year	Master of Science Thesis Titles
Arthur, B.	1987	*Treatment of Iron, Chromium, and Nickel Aqueous Chloride Acidic Solutions by Phosphate Precipitation*
Rapkoch, J.	1987	*The Effects on Metal Phosphate Precipitation from Complex Solutions by Substituting Sodium Hydroxide, the Titrant, with Ammonium Hydroxide*
Quinn, J.	1988	*Conversion of Chromium Phosphate to Chromic Acid by Fusion Process*
Donelon, D.	1989	*Recovery of Metal Values from Spent Stainless Steel Pickle Liquors*
Flynn, D.	1990	*Treatment of Electromachining Waste for Selective Nickel/Cobalt Separation*
Leary, R.	1990	*Treatment of Stainless Steel Pickling Liquors*
McGrath, S.	1992	*The Rate of Precipitation of Chromium Phosphate*
Shuey, S.	1992	*Survey of Techniques for the Separation of Cobalt and Nickel*

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APPENDIX A. Stability diagrams as a function of pH for Phosphate Compounds (the source of thermodynamic data for phosphate species is discussed by Konda (1986) in his M.Sc. Thesis)

Trivalent Metal Species: Iron, Chromium, Aluminum

(Figure numbering follows that used in the publications **Twidwell, L.G., D.R. Dahnke. 1986.** *Metal Value Recovery from Alloy Chemical Milling Waste:* EPA Contract Number 68-02-4172. March, 184p. **Twidwell, L.G., D.R. Dahnke. 1987.** *Metal Value Recovery from Alloy Chemical Milling Waste: Phase II.* EPA Contract Number 68-02-4432. December, 189p)

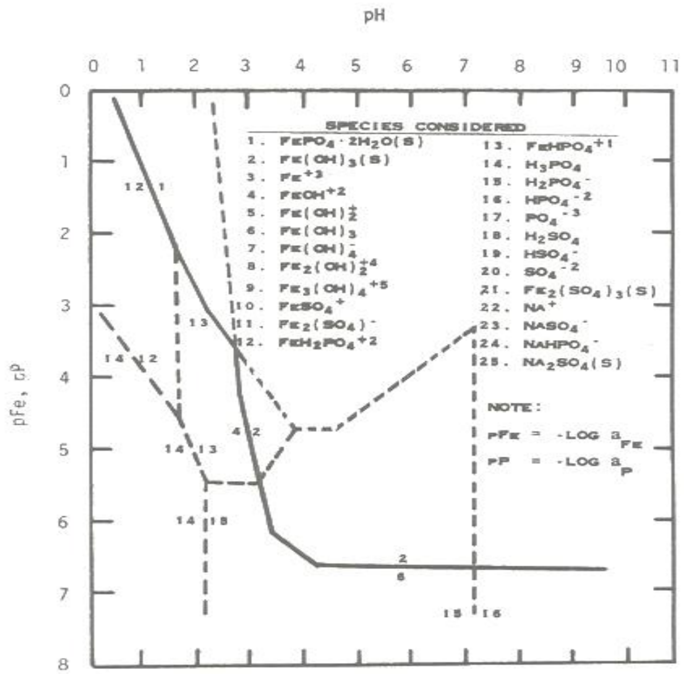


Figure 1.1. Ferric Phosphate stability diagram for the Ferric/Phosphate/ Sulfate/Water system [Twidwell and Dahnke, 1987, page 7; Dahnke, 1985. Konda, 1987] (see Konda for presentation of the sources of thermodynamic data and calculation of specie stability free energies)

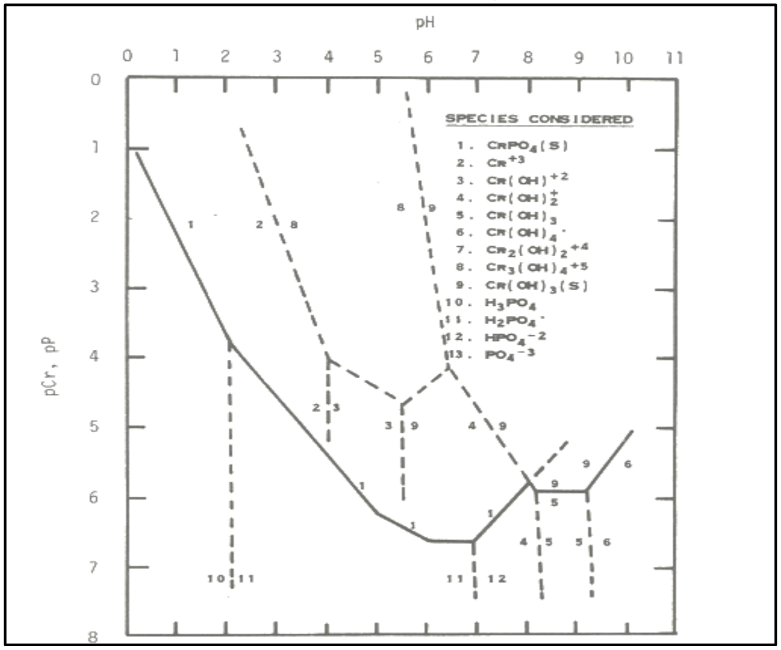


Figure 1.2. Chromium Phosphate stability diagram for Chromium/Phosphate/ Water System [Twidwell and Dahnke, 1987 page 8; Dahnke, 1985; Konda, 1987]

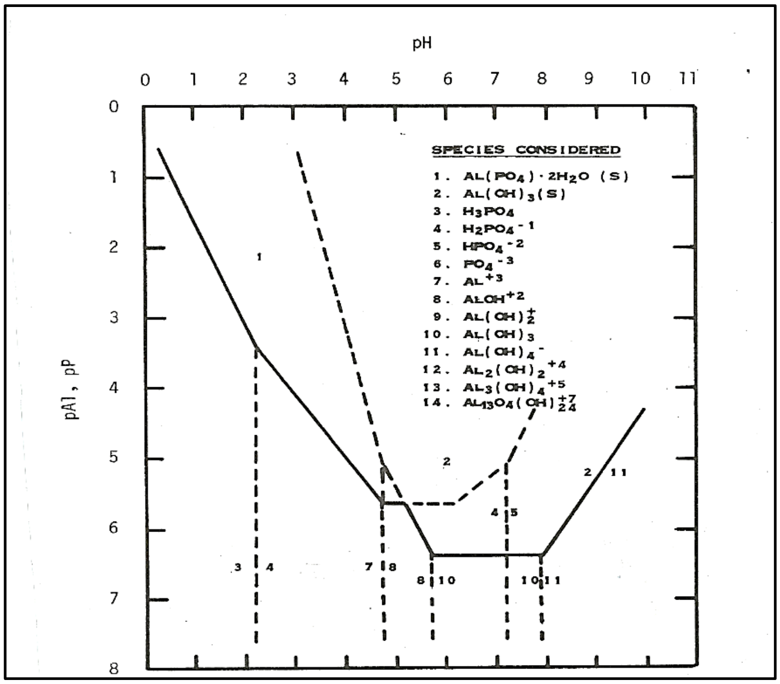


Figure 1.3. Aluminum Phosphate stability diagram for the Aluminum/Phosphate /Water system ([Twidwell and Dahnke, 1987; page 8; Dahnke, 1985; Konda, 1987]

Divalent Metal Species: Cadmium, Ferrous, Nickel, Zinc

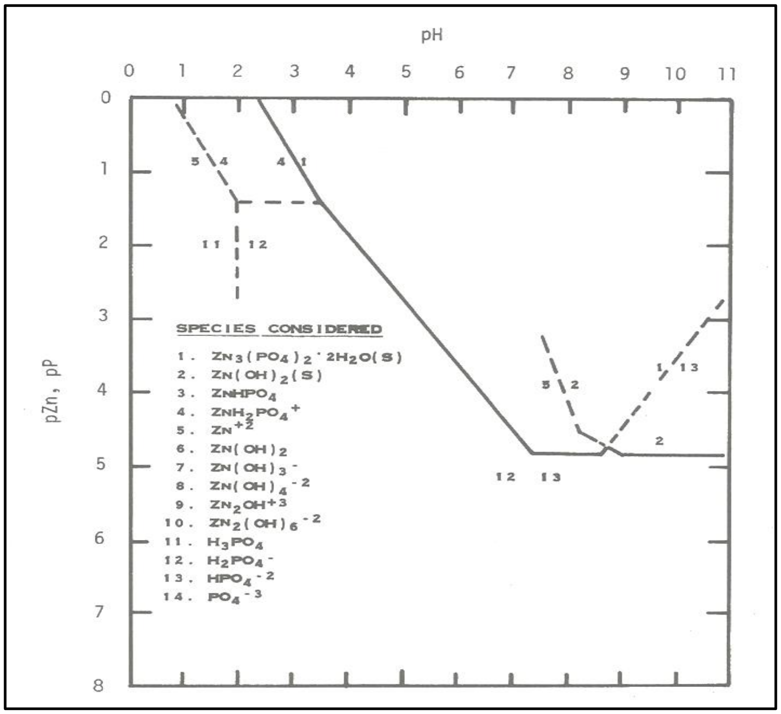


Figure 1.4. Zinc Phosphate stability diagram for the Zinc/Phosphate/Water system [Twidwell and Dahnke, 1987; Dahnke, 1985 page 10; Konda, 1987]

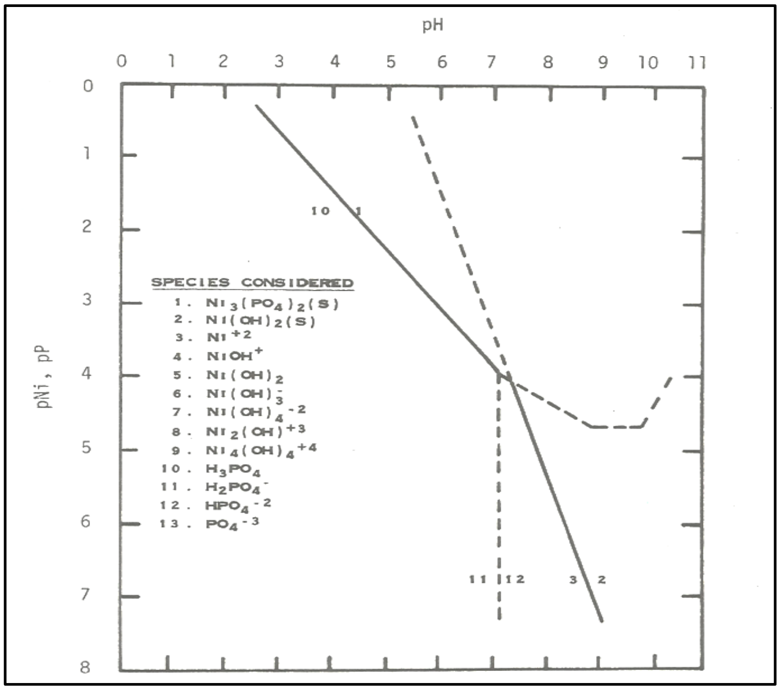


Figure 1.5. Nickel Phosphate stability diagram for the Nickel/Phosphate/Water system [Twidwell and Dahnke, 1987; Dahnke, 1985; Konda, 1987]

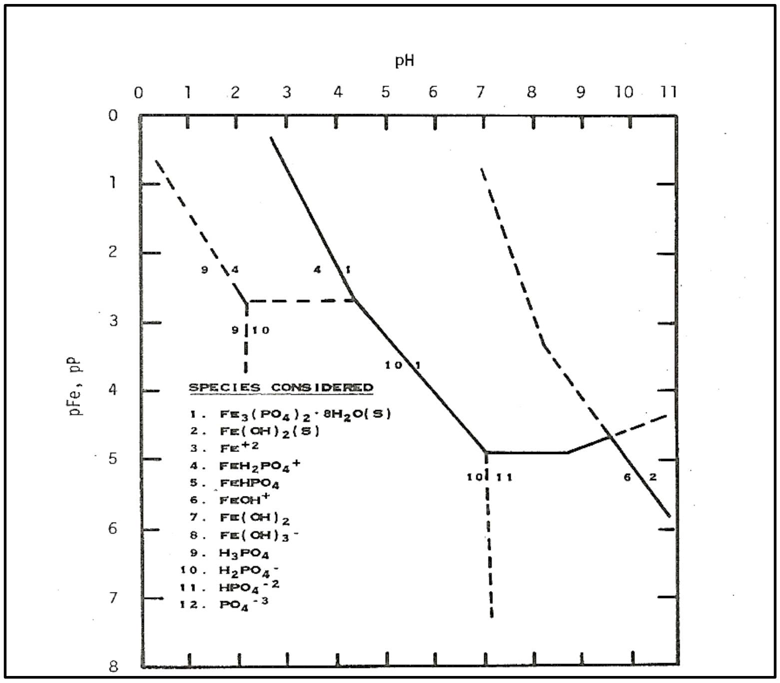


Figure 1.6. Ferrous Phosphate stability diagram for the Ferrous/Phosphate/Water system [Twidwell and Dahnke, 1987; Dahnke, 1985; Konda, 1987]

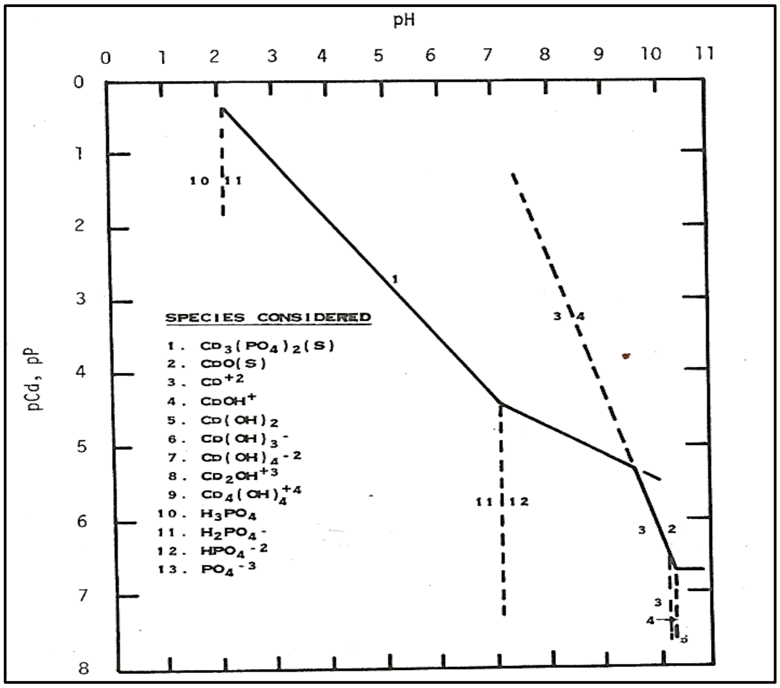
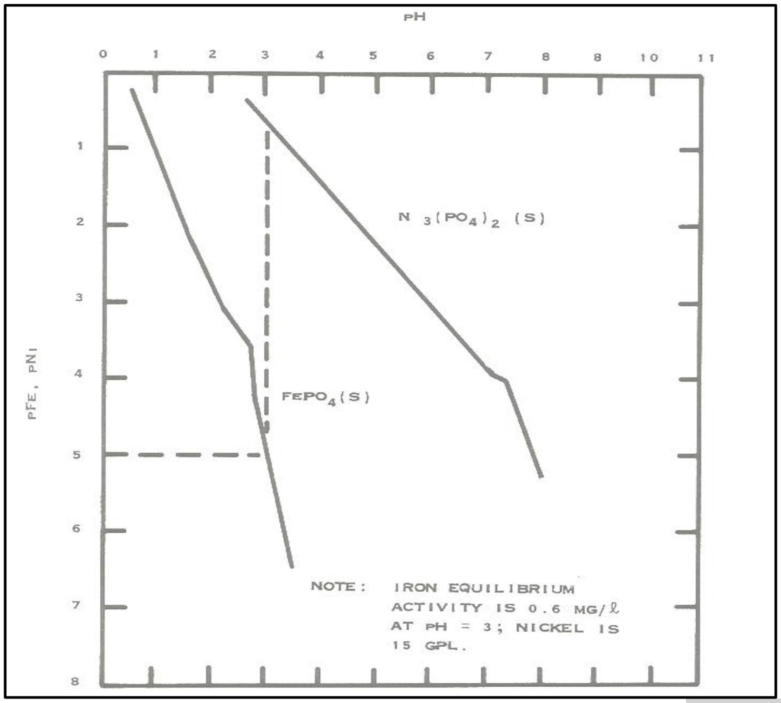


Figure 1.7. Cadmium Phosphate stability diagram for the Cadmium/Phosphate/Water system [Twidwell and Dahnke, 1987; Dahnke, 1985; Konda, 1987]



NOTE: IRON EQUILIBRIUM ACTIVITY IS 0.6 MG/ℓ AT PH = 3; NICKEL IS 15 GPL.

Figure 1.8. Ferric removal from Nickel by Phosphate Precipitation [Twidwell and Dahnke, 1987; Dahnke, 1985; Konda, 1987]

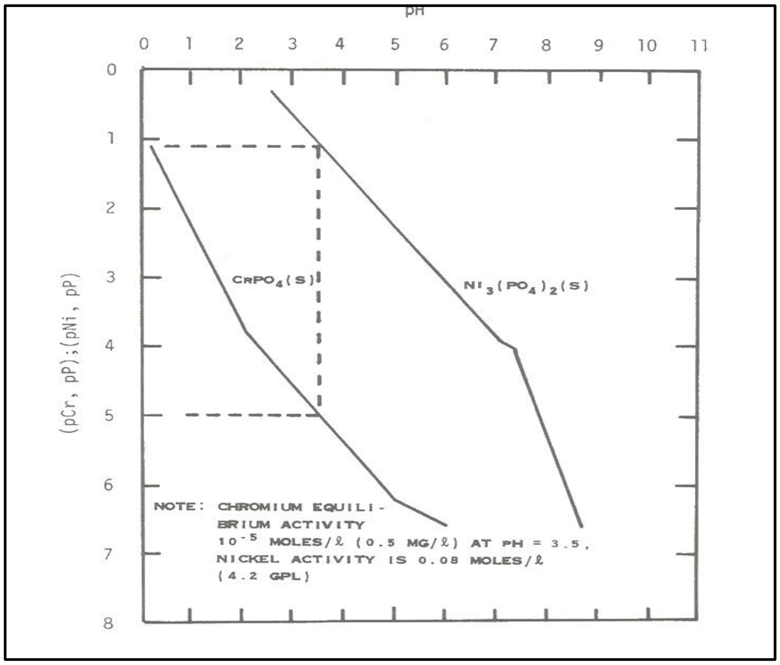
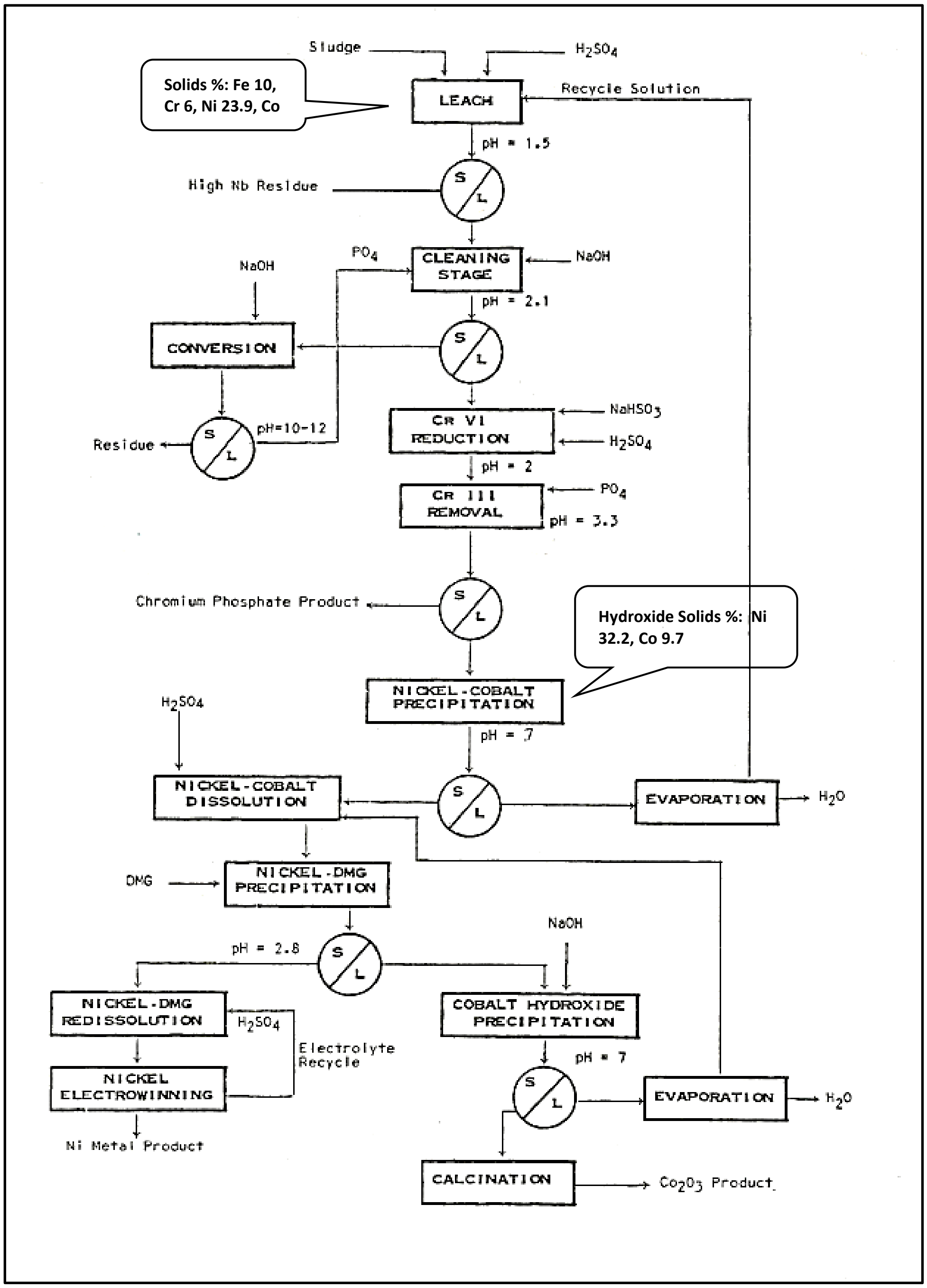


Figure 1.9. Chromium removal from Nickel by Phosphate precipitation [Twidwell and Dahnke, 1987; Dahnke, 1985; Konda, 1987]

APPENDIX B. Example Treatment Sequence Flowsheet

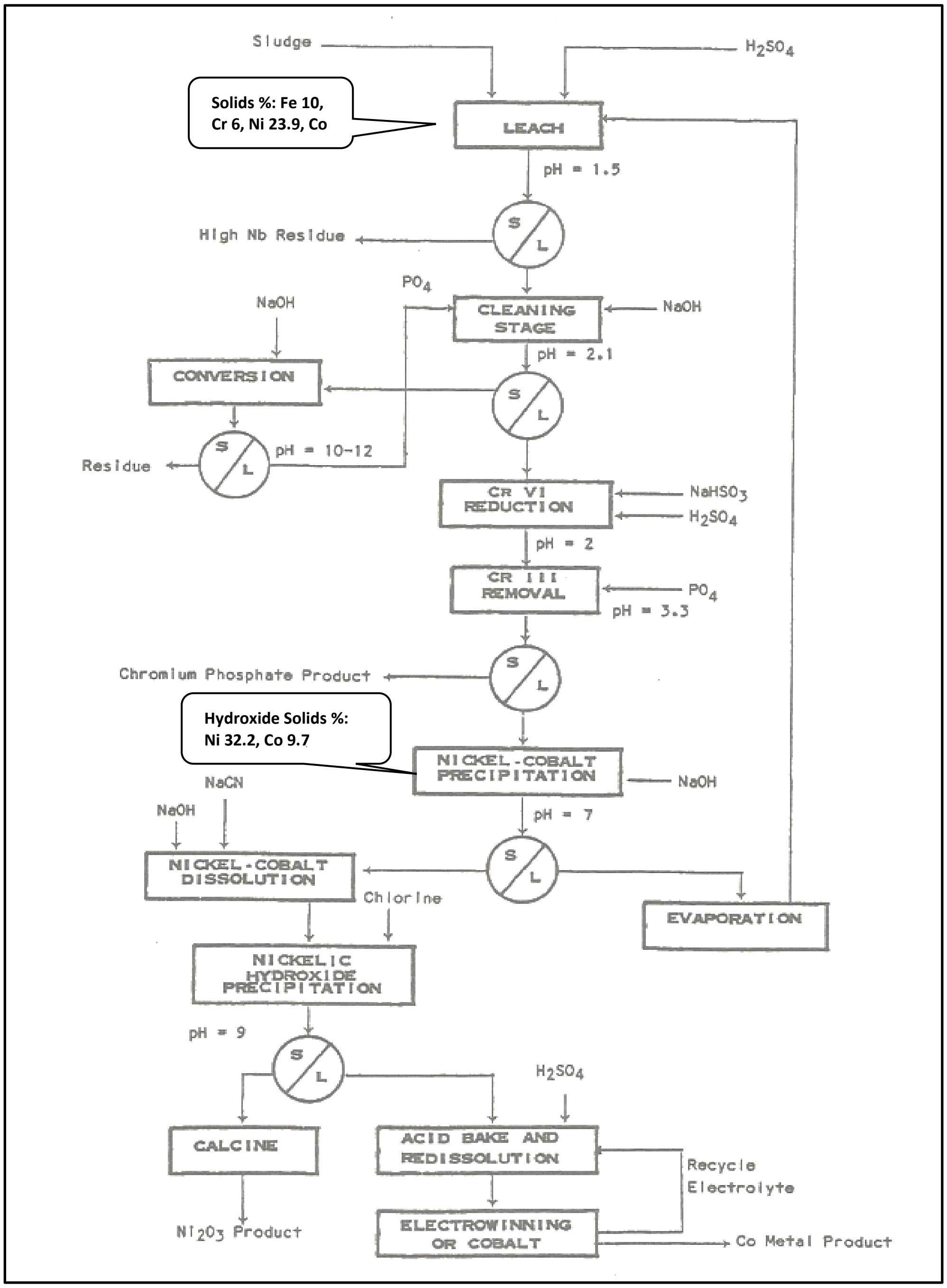
(Figure numbering follows that used in the publication. **Twidwell, L.G., D.R. Dahnke. 1987.** *Metal Value Recovery from Alloy Chemical Milling Waste: Phase II.* EPA Contract Number 68-02-4432. December, 189p)



Solids %: Fe 10, Cr 6, Ni 23.9, Co

Hydroxide Solids %: Ni 32.2, Co 9.7

Figure 2.2. Treatment Sequence for Cobalt (~5%)/Nickel (~24%) bearing Electrochemical Sludge using the Dimethylglycime (DMG) Process [Twidwell and Dahnke, 1987, page 6]



Solids %: Fe 10, Cr 6, Ni 23.9, Co

Hydroxide Solids %: Ni 32.2, Co 9.7

Figure 2.3. Treatment Sequence for Cobalt (~5%)/Nickel (~24%) bearing Electrochemical. Sludge using the Cyanide Double Salt Process for Separating High Purity Nickel and Cobalt [Twidwell and Dahnke, 1987, page 7]

APPENDIX C. Master Science Theses by the Twidwell Research Team (Part 2 thesis authors are highlighted in the following table)

Author	Year	Master of Science Thesis Title
Hohn, J.	2005	Hohn, J., *Arsenic Removal by Modified Ferrihydrite Adsorption*
Dufrense, R.	1974	*Leach of Copper Reverberatory Slag*
Knoepke, J.	1974	*Treatment of copper dross flue dust for the extraction of Arsenic*
Hwang, J.	1975	*Lime Roast and Leach of Sulfuric Acid Treated Copper Reverberatory Slag*
Mehta, A.	1976	*Fixation of Arsenic in copper smelter flue dust*
Mansanti, J.	1978	*The Precipitation of Iron as a Jarosite from Iron, Copper, and Zinc Containing Solutions*
Flynn, H.	1980	*Treatment of Lead Smelter Speiss*
Blaskovich, S.	1982	*Elemental Distribution of Lime-Roasted Lead Smelter Speiss in a Copper Matte-Slag System*
Roset, G.	1982	*The Influence of Experimental Variables on the Elemental Distribution of Lime-Roasted Smelter Dusts in a Copper Matte-Slag System*
Downey, J.	1982	*Elemental Distribution of Lime-Roasted Smelter Dusts in a Copper Matte-Slag System*
Anderson, C.	1982	*A Survey of Roasting Techniques to Volatilize Arsenic and Antimony from Copper Smelter*
Downey, J.	1982	*Separation and Recovery of Chromium and Nickel from Mixed Metal Solutions*
Laney, D.	1984	*The Application of Solvent Extraction to Complex Metal Bearing Solutions*
Newhouse, J.	1984	*Segregation Process Applied to Copper Smelter Flue Dust*
Peterson, M.	1985	*Treatment of Lead Smelter Speiss*
Dahnke, D.	1985	*Removal of Iron from Process Solutions*
Arratia, J.	1985	*Optimization of Copper Recovery from Smelter Flue Dust*
Fitzpatrick, G.	1986	*The Influence of Additive Compounds on Copper Segregation*
Nordwick, S.	1987	*Conversion of Precipitated Ferric Phosphate to Ferric Hydroxide*
Arthur, B.	1987	*Treatment of Iron, Chromium, and Nickel Aqueous Chloride Acidic Solutions by Phosphate Precipitation*
Abbas, M.H.	1987	*Formation and stability studies of some iron-arsenic and copper-arsenic compounds (Hsin Huang was thesis advisor)*
Comba, P.	1987	*Removal of Arsenic from Process and Wastewater Solutions*
Rapkoch, J.	1988	*The Effects on Metal Phosphate Precipitation from Complex Solutions by Substituting Sodium Hydroxide, the Titrant, with Ammonium Hydroxide*
Quinn, J.	1988	*Conversion of Chromium Phosphate to Chromic Acid by Fusion Process*
Neira, M.	1990	*Recovery of Elemental Arsenic from Copper Smelter Flue Dust by Volatilization*
Flynn, D.	1990	*Treatment of Electromachining Waste for Selective Nickel/Cobalt Separation*
Leary, R.	1990	*Treatment of Stainless Steel Pickling Liquors*
Honoras, C.	1992	*Recovery of Copper and Zinc from Copper Reverberatory Slags*
McGrath, S.	1992	*The Rate of Precipitation of Chromium Phosphate*
Shuey, S.	1992	*Survey of Techniques for the Separation of Cobalt and Nickel (Selective Separation of Nickel and Cobalt from Electro-machining Sludges)*
Dover, L.	1992	*Treatment of Chromium Contaminated Soils*
Tang, X.	1992	*Recovery of Copper from Copper Smelter Flue Dust*
Plessas, K.	1992	*Recovery of Arsenic from Process Wastewaters*
Shi, Y.	1992	*Treatment of acid mine drainage at the Berkely Pit, Butte, Montana by Chemical Precipitation (Hsin Huang was thesis advisor)*
Pande, P.	1993	*Lead Blast Furnace and Dezinced Slag Stability*
Krishnan, S.	1994	*Arsenic Removal by Soil Washing*
Weldon, T.	1994	*Slag Chemistry Refining of Molten Stainless Steel*
Gensler, C.	1994	*Stability of Lime-Initiated Hydroxide Precipitation Sludge*

Author	Year	Master of Science Thesis Title
Liu, C.	1994	*Bench scale chemical Treatability Study of Berkeley Pit Water in Mine Waste, Pilot Program (Hsin Huang was thesis advisor)*
Miranda, P.	1996	*Removal of Arsenic from Wastewaters as Stable Iron Mineral Compounds*
Saran, J.	1997	*Removal of Arsenic from Berkeley Pit Wastewater and Long-Term Stability of the Product Solids*
Wilson, S.	1998	*Removal of Arsenic from ASARCO Blow-Down Water and Long-Term Stability of the Product Solids*
Gale, M.	1998	*Removal of Arsenic from Wastewaters by Iron/Phosphate Precipitation*
Dahlgren, E.	2000	Dahlgren, E. *Parameters Affecting the Cementation of Selenium from Wastewaters*
Williams-Beam	2001	*Technologies for the Recovery of Thallium from Wastewaters*
Orser, T.	2001	*Removal of Arsenic from Wastewaters as Stable Calcium Mineral Compounds*
Hadden, G.	2002	*Rate of Removal of Oxyanions of Arsenic and Selenium from Mine Wastewater using Galvanically Enhanced Cementation*
Sundberg, J.	2003	*Removal of Heavy Metals from Wastewater by Reductive Precipitation*
Leonhard, J.	2006	Heavy Metals *Removal by Modified Ferrihydrite Adsorption*
Glasgow, M.	2007	*Modified Ferrihydrite/Arsenic: Effect of Anions*

Appendix D. Treatment of Electroplating and Electromachining Sludges (1983 to 2001)

Researcher	Reference	Publication
Laney, D.	M.Sc. Thesis (1984) *The Application of Solvent Extraction to Complex Metal Bearing Solutions*	
Twidwell, L.G., A. Mehta, G. Hughes	*Metal Value Recovery from Metal Hydroxide Sludge*	EPA-60019-84-022, Sept. 1984, pp. 129-133.
Dahnke, D.	M.Sc. Thesis (1985) *Removal of Iron from Process Solutions*	
Dahnke, D. R., L. G. Twidwell, B. W. Arthur and S. M. Nordwick	*Selective Recovery of Metal Values from Electroplating Sludge by the Phosphate Process*	Proceedings of SUR/FIN-86, 73rd AESF Annual Technical Conference, Philadelphia, PA, June 23-26, 1986, Session C-3, 20 p.
Dahnke, D. R., L. G. Twidwell, B. W. Arthur and S. M. Nordwick	Recovery of Metal Values from Metal-Finishing Hydroxide Sludges by Phosphate Precipitation	12th Annual Hazardous Waste Symposium, Cincinnati, Ohio, April 21-23, 1986
Downey, J.	M.Sc. Thesis (1986) *Separation and Recovery of Chromium and Nickel from Mixed Metal Solutions*	
Konda, Ed A.	M.Sc. Thesis (1986) *Ferric Phosphate Precipitation as a Means of Iron Removal from Zinc Bearing Acidic Aqueous Solutions*	
Twidwell, L.G., D.R. Dahnke, W.L. Huestis, J. P. Quinn, P.G. Comba	*Pilot Scale Results of Metal Value Recovery from Mixed Metal Hydroxide Sludge*	Proceeding's 8th AESF/EPA Conference on Pollution Control for the Metal Finishing Industry, San Diego, CA, February 9-11, 1987.
Nordwick, S.	M.Sc. Thesis (1987) *Conversion of Precipitated Ferric Phosphate to Ferric Hydroxide,*	
Arthur, B.	M.Sc. Thesis (1987) *Treatment of Iron, Chromium, and Nickel Aqueous Chloride Acidic Solutions by Phosphate Precipitation*	

Researcher	Reference	Publication
Twidwell, L.G., D.R. Dahnke	*Metal Recovery from Electroplating Waste*	Proceedings of the First International Conference on Hydrometallurgy, (ICHM '88), Edited by Z. Yulian, X. Jiazhong, Beijing, China, October 1988, International Acad. Publishers, pp. 394-388.
Twidwell, L.G., D.R. Dahnke	*Treatment of Metal Finishing Sludge for Detoxification and Metal Value Recovery*	EJMPEP, Vol 1, No 2, 2001, pp 76-88.
Rapkoch, J.	M.Sc. Thesis (1988) *The Effects on Metal Phosphate Precipitation from Complex Solutions by Substituting Sodium Hydroxide, the Titrant, with Ammonium Hydroxide*	
Quinn, J.	M.Sc. Thesis (1980) *Conversion of Chromium Phosphate to Chromic Acid by Fusion Process*	
Twidwell, L.G., D.R. Dahnke, S.F. McGrath	*Detoxification of and Metal Value Recovery from Metal Finishing Sludge Materials*	Innovative Hazardous Waste Treatment Technology Series, Volume 2, Physical Chemical Processes, Editor H. M. Freeman, Technomic Publishing Company, 1990, pp. 56-62.
Flynn, D.	M.Sc. Thesis (1990) *Treatment of Electromachining Waste for Selective Nickel/Cobalt Separation*	
Flynn, D.R., L.G. Twidwell	*Selective Recovery of Nickel and Cobalt from Electromachining Process Solutions*	Copper, Nickel, Cobalt Metallurgy, AIME Symposium, New Orleans, LA, February 1991.
Dahnke, D.R., D. Flynn, S.A. Shuey, L.G. Twidwell	*Selective Recovery of Metal Values from Electrochemical Machining Sludge: Recovery of Cobalt*	Eighteenth Annual Risk Reduction Engineering Laboratory Research Symposium, EPA/600/R-92/028, Cincinnati, OH, April 14-16, 1992, pp. 96-100.
McGrath, S.	M.Sc. Thesis (1992) *The Rate of Precipitation of Chromium Phosphate*	
Shuey, S.	M.Sc. Thesis (1992). *Selective Separation of Nickel and Cobalt from Electromachining Sludges*	
Twidwell, L.G., S.A. Shuey, D.R. Flynn, D.R. Dahnke	*Selective Recovery of Nickel and Cobalt from Electromachining Sludge Materials*	J. Haz. Waste and Haz. Mat., Vol. 10, No. 4, 1993, pp 297-311.

APPENDIX E. List of Presentations and Publications by the Twidwell Research Group (treatment of electroplating and electromachining sludges are highlighted in the following information)

LARRY G. TWIDWELL (Professor Emeritus)

[Contact Information: 1300 W. Park Street, Butte, Montana; 406 560 2263, ltwidwell@mtech.edu, enviromet1@gmail.com; Engineering Classroom Building (ELC-216); Metallurgical and Materials Engineering Department, Montana Technological University, 1300 W. Park, Butte, Montana]

Brief Bio

Larry G. Twidwell, D.Sc. is Emeritus Professor in the Department of Metallurgical and Materials Engineering at Montana Tech. He has forty-five years of experience in teaching and directing research in Metallurgical Engineering at Montana Tech. Twidwell and his graduate students and coworkers have conducted research emphasizing extractive metallurgy and the application of extractive metallurgical engineering to the treatment of metallurgical wastes, process waters and by-products. Four books, fifty-eight theses, one hundred twenty-seven publications and one hundred ten national and international presentations have resulted from their research efforts. Twidwell has received several outstanding teacher/researcher awards during his tenure at Montana Tech, e.g., TMS-EPD Distinguished Lecturer Award, 2011; TMS-EPD Best Technology Paper Award, 2006; AIME Frank Aplan Award, 2004; Montana Tech Lifetime Distinguished Researcher Award, 2002; AIME Mineral Industry National Education Award, 2001; Montana Academy of Sciences Mershon Award as Outstanding Montana Researcher, 1989; Outstanding Scholar Award, Montana Tech, 1985; and Outstanding Educator Awards, Montana Tech, 1970, 1971, 1973, 1974.

Technical Presentations (metal hydroxide electroplating and electromachining sludge references are highlighted)

1. Montana Society of Engineers, Feb. 1974, *Recovery of Metals from Reverberatory Slags*, Butte, Mt. (Presenter: **L.G. Twidwell**).
2. Society of Exploration Geophysicists, Dec. 1975, *Self-Paced Tutorial Instruction.* (Presenter: **L.G. Twidwell**).
3. American Society for Engineering Education, June 1978, *Self-Paced Instruction on Extractive Metallurgy,* Vancouver, WA. (Presenter: **L.G. Twidwell**).
4. American Institute of Chemical Engineers, Nov. 1978, *Fixation of Arsenic in Copper Smelter Flue Dust by Lime Roasting* (co-authors: A. Mehta, J. Burckle), Atlanta, GA. (Presenter: **L.G. Twidwell**).
5. INDO-U.S. Workshop on Mineral Processing and Chemical Metallurgy, *AMAX Segregation Process: The Distribution of Impurities, Recovery of Metal Values and Disposal of Arsenic from Smelter Flue Dusts,* Proceedings INDO-U.S. Workshop on Mineral Processing and Chemical Metallurgy, Dec. 14-17, 1981, Udaipur, India, pp. 184-85. (Presenter: **L.G. Twidwell**)
6. American Institute of Mining, Metallurgical Engineers, Feb. 1984, *Segregation Applied to Copper Concentrate: Distribution of Impurities,* 113th Annual Meeting, Los Angeles, CA (Presenter: **L.G. Twidwell**, Co-author: K. Beuerman).
7. Tenth Annual Research Symposium Land Disposal, Incineration and Treatment of Hazardous Waste, April 1984, *Recovery of Metals from Electroplating Sludge,* (Presenter: **L.G. Twidwell**, Co-authors: A. Mehta, G. Hughes), Cincinnati, OH.
8. California Environmental Health and Safety Annual Meeting, May 1984, *Recovery of Metal Values from Electroplating Wastes, Phase II,* (Presenter: **L.G. Twidwell**, Co-authors: A. Mehta, G. Hughes), Sacramento, CA.
9. American Institute of Mining, Metallurgical Engineers, March 1986, *Treatment of Speiss for Metal Value Recovery,* 115th Annual Meeting, (Presenter: **L.G. Twidwell**, Co-author: M. Peterson) New Orleans, LA.
10. Twelfth Annual Hazardous Waste Symposium, April 21-23, 1986, *Recovery of Metal Values from Metal Finishing Hydroxide Sludge: A Project Summary,* (Presenter: **L.G. Twidwell**, Co-authors D. Dahnke, B. Arthur, S. Nordwick) Cincinnati, OH.
11. SUR/FIN '86, American Electroplating and Surface Finishing Conference, June 1986, *Selective Recovery of Metal Values from Electroplating Hydroxide Sludge by the Phosphate Process,* ((Presenter: **L.G. Twidwell**, Co-authors: D. Dahnke, B. Arthur, S. Nordwick) Philadelphia, PA.
12. European Economic Commission Symposium, May 27-28, 1986, *Disposal of Arsenic Bearing Waste Material and Smelter By-Product,* (Presenter: **L.G. Twidwell**, Co-authors: M. Peterson, P. Comba) University of Maryland.

13. International Symposium on Solubility, August 1986, *Solubility Diagrams for Aqueous Metal Phosphate Systems,* (Presenter: **L.G. Twidwell**, Co-author: R. G. Robins, D. R. Dahnke) Newark, NJ.
14. International Symposium on Iron Control in Hydrometallurgy, CIM, October, 1986, *Selective Iron Removal from Process Solutions by Phosphate Precipitation,* (Presenter: **L.G. Twidwell**, Co-authors: D. Dahnke and R. Robins) Toronto, Canada.
15. 116th AIME Annual Meeting, February 23-26, 1987, *Removal of Arsenic from Process and Wastewater Solutions,* (Presenter: **L.G. Twidwell**, Co-authors: P. G. Comba, D. R. Dahnke) Denver, CO.
16. Pacific Northwest Metals and Minerals Conference, April 27-28, 1987, *Treatment of Electroplating Sludge Material for Metal Recovery,* (Presenter: **L.G. Twidwell**, Co-author: J. Quinn).
17. Pacific Northwest Metals and Minerals Conference, April 27-28, 1987, *Removal of Arsenic from Process and Wastewaters,* (Presenter: **L.G. Twidwell**, Co-author: P. G. Comba) Portland, OR.
18. Annual Meeting USBM Generic Center for Mineral Industry Waste Treatment, May 1987, *Removal of Arsenic from Process and Wastewater Solutions,* (Presenter: **L.G. Twidwell**, Co-author: P. G. Comba) Socorro, NM.
19. 117th AIME Annual Meeting, January 25-28, 1988, *Removal of Arsenic from Process and Wastewater Solutions: Update,* (Presenter: **L.G. Twidwell,** Co-authors: P. G. Comba, D. R. Dahnke) Phoenix, AZ.
20. First International Conference on Hydrometallurgy, October 1988, *Metal Recovery from Electroplating Waste,* Beijing, China, (Presenter: **L.G. Twidwell**, Co-author D. R. Dahnke)
21. Annual Meeting USBM Generic Center for Mineral Industry Waste Treatment, June 1989, *Removal of Arsenic from Wastewaters,* (co-author T. Bowler) Reno, NV (Presenter: **L.G. Twidwell**)
22. Annual Meeting USBM Generic Center for Mineral Industry Waste Treatment, June 1989, *Recovery of Metal Values from Stainless Steel Pickling Liquors,* Reno, NV. (Presenter: **L.G. Twidwell**, Co-author: D. Donelon)
23. Sabbatical Presentations, Jan. - June 1990, *Removal and Stabilization of Arsenic Wastes*, Tohoku Engineering Faculty (Sendai, Japan), Government Institute for Research (Sendai, Japan), Akita University Engineering Faculty (Akita, Japan), Akita Zinc Smelter (Akita, Japan), Mitsubishi Copper Company (Naoshima, Japan), EZ Zinc (Hobart, Tasmania), Australian Nuclear Science and Technology Organization (Sydney, Australia), Mt. ISA Mining and Minerals (Mt. ISA, Australia). (Presenter: **L.G. Twidwell**).
24. Annual Meeting USBM Generic Center for Mineral Industry Waste Treatment, June 1990, *Survey Techniques to Treat Stainless Steel Pickling Liquors* (co-author R. Leary), Reno, NV. (Presenter: **L.G. Twidwell**).
25. 1990 Minerals and Hazardous Waste Symposium, October 1990, *Recovery of Chromium from Electroplating Solutions*, Butte, MT. (Presenter: **L.G. Twidwell**, Co-authors: S. F. McGrath, D. R. Dahnke, B. A. Arthur),
26. 1990 Mineral and Hazardous Waste Processing Symposium, October 1990, *Removal of Arsenic from Process Solutions and Stabilization of Solids*, Butte, MT. (Presenter: **L.G. Twidwell**)
27. 119th Annual AIME Meeting, EPD CONGRESS 1991, Extractive Metallurgy of Copper, Nickel, Cobalt, Feb. 1991, *Selective Recovery of Nickel and Cobalt from Electromachining Process Solutions.* New Orleans, LA, (Presenter: **L.G. Twidwell,** Co-author D. R. Flynn),
28. 119th Annual AIME Meeting, EPD CONGRESS 1991, Extractive Metallurgy of Copper, Nickel, and Cobalt, Feb. 1991, *Solubility of Metal Phosphates*, (Presenter: **L.G. Twidwell**, Co-authors: R. G. Robins, D. R. Dahnke, S. F. McGrath, and G. H. Khoe)
29. Montana Academy of Science, Treating Contaminated Soils and Water, Bozeman, MT, March 27, 1992, *Treatment of Chromium Contaminated Soils,* (Presenter: **L.G. Twidwell,** Co-author: L. Dover).
30. Eighteenth Annual Risk Reduction Engineering Laboratory Research Symposium, EPA, Cincinnati, OH, April 14-16, 1992, *Recovery of Metal Values from Electrochemical Machining Sludge*, . (Presenter: **L.G. Twidwell**), Co-authors: D. R. Dahnke, D. FLynn, S. Shuey).
31. Spectrum 92, Boise, Idaho, August 1992, *Slag Chemistry and Metals Volatilization in the Plasma Arc Furnace Experiment*, (Presenter: **L.G. Twidwell**, Co-authors: C. G. Whitworth, T. W. Jenkins, G. F. Wyss).
32. Mine Waste Management & Remediation Conference, Butte, MT, July 7-9, 1992, *Removal of Arsenic from Wastewaters and Stabilization of Arsenic Bearing Waste Materials. .* (Presenter: **L.G. Twidwell**).
33. Cooperative Research Center, Stabilization of Arsenic Waste, Sydney, Australia, July 20, 1992, *Recovery of Metal Values from Mineral Processing and Electro-finishing Waste.* (Presenter: **L.G. Twidwell**).

34. EPA Workshop on ARSENIC, Washington, DC, August 17-17, 1992, *Removal of Arsenic from Wastewaters and Stabilization of Arsenic Bearing Waste Solids,* (Presenter: **L.G. Twidwell**, Co-authors: K. O. Plessas, T. P. Bowler).
35. EPA Workshop on MERCURY, Washington, DC, August 19-20, 1992, *Hydrometallurgical Process for Mercury Recovery from F106 Muds*, (Presenter: **L.G. Twidwell,** Co-author: M. A. Rockandel).
36. Mine Closure Short Course, Helena, MT, April 27-29, 1993, *Arsenic and Heavy Metal Mobility Considerations*, (Presenter: **L.G. Twidwell,** Co-author H.H. Huang).
37. Australian Water and Wastewater Association, Sydney, Australia, May 27, 1993, *Mine Waste Environmental Research Programs.* (Presenter: **L.G. Twidwell**).
38. Murdock University, Perth, Australia, June 1, 1993, *Removal of Arsenic from Wastewaters and Stabilization of Arsenic Bearing Waste Materials.* (Presenter: **L.G. Twidwell**).
39. Mine Waste Center Arsenic Seminar, November 4, 1994, *Removal of Arsenic from Mine Water"*, Montana Tech, Butte, Mt. (Presenter: **L.G. Twidwell**).
40. Australian Nuclear Science and Technology Organization (ANSTO), February 9, 1994, *Decontamination of Radioactive Scrap Stainless Steel by Melt/Slag Refining.* (Presenter: **L.G. Twidwell**).
41. SME-AIME Annual Meeting, Albuquerque, NM, Feb. 15, 1994, *Recovery of Silver from Manganiferous Silver Ores by Segregation Roasting-Flotation*. (Presenter: T.J. Jordan, Coauthors: C. Flores, **L.G. Twidwell**).
42. Montana Academy of Sciences, Montana Tech, Butte, MT, April 15-16, 1994, *Treatment of Anaconda Smelter Site Soil for Arsenic Removal*, (Presenter, S. Krishnan, Co-author: **L.G. Twidwell**).
43. Montana Academy of Sciences, Montana Tech, Butte, MT, April 15-16, 1994, *Bioleaching of Arsenopyrite*, (Presenter D. Anderson, Co-author: **L.G. Twidwell**).
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60. University Concepcion, May 9-13, 2000, *The Removal of Arsenic from Hydrometallurgical Process and Effluent Streams*, International Conference on Clean Technology for the Mining Industry, Santiago, Chile (Presenter, T. Nishimura, Co-authors: R.G. Robins, **L.G. Twidwell**).
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75. SME, March 2005, *Removal of Selenium Oxyanions from Mine Waters Utilizing Elemental Iron and Galvanically Coupled Metals*, J.D. Miller Symposium, Innovations in Natural Resource Systems, Salt Lake City, UT, (**L.G. Twidwell,** Co-authors: J.M. McCloskey, H. Joyce, E. Dahlgren, A. Hadden).
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82. COM, October 2006, *A Comparison of Ferrihydrite and Aluminum Modified Ferrihydrite for Removing Arsenate by Co-Precipitation*, Iron Control in Hydrometallurgy, CIM, Montreal, (Presenter, J. Hohn, Co-authors: **L.G. Twidwell**, R.G. Robins).
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89. Hydrometallurgy 2008, August 2008, *Free Energies from The Solubility of Solid Compounds Using Speciation Calculations,* SME/TMS/CIM Fall Meeting, Phoenix, AZ, August 2008, (Presenter: H.H. Huang, Co-authors: **L.G. Twidwell**, C.A. Young, R.N. Gow, J. McCloskey)
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