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Processing of Waste Solutions From Electrochemical Decontamination

L. A. Charlot
R. P. Allen
H. W. Arrowsmith
J. L. Hooper

September 1979

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Pacific Northwest Laboratory
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Pacific Northwest Laboratory
Richland, Washington 99352

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SUMMARY

Large quantities of surface-contaminated metallic waste are generated by operating nuclear fuel cycle facilities, by the decommissioning of retired facilities, and by the processing of defense materials. This metallic waste, and particularly that contaminated with transuranic elements, will require expensive handling, storage and, ultimately, geologic disposal. Research conducted at Pacific Northwest Laboratory, operated by Battelle Memorial Institute for the Department of Energy, has shown that electropolishing is a large-scale decontamination technique that can rapidly and economically remove transuranic and other radionuclide contamination from metal surfaces. The successful development and widespread application of this decontamination technique would permit a substantial reduction in the volume of metallic waste requiring expensive perpetual care or geologic disposal. Other benefits include minimization of personnel exposure, reduced risk of environmental contamination, and the preservation of large quantities of irreplaceable metals and alloying elements for possible future use.

However, the use of electropolishing as a decontamination technique will only be an effective process if we can minimize the amount of secondary waste requiring disposal and economically recycle part of the decontamination electrolyte. Consequently, a solution purification method is needed to remove the dissolved contamination and metal in the electrolyte. This report describes the selection of a purification method for a phosphoric acid electrolyte from the following possible acid reclamation processes:

- ion exchange
- solvent extraction
- precipitation
 - alcohol precipitation
 - neutralization
 - dilution
 - sulfide precipitation
 - potassium or barium salt precipitation

- distillation
- electrolysis
- membrane separation

Studies show that the most promising purification methods are ion exchange and solvent extraction. Tests of the effectiveness of ion exchange as a solution processing approach have been conducted by the manufacturer of a commercial acid purification system using a synthetic spent 75 wt% phosphoric acid electrolyte containing 3 wt% stainless steel impurities. The results indicated that the full strength spent acid could be purified at a scaled flow rate of about 40 gal/hr with about a 40% decrease in impurity content.

The advantages of this ion exchange (strong acid adsorption) method over solvent extraction include

- availability of an inexpensive commercial system
- flexible unit operation
- ability to achieve adequate impurity removal without the addition of expensive or potentially hazardous processing chemicals.

An alternative method to strong acid adsorption is purification by solvent extraction. Experimental results show that this method cleans the acid and completely removes plutonium with acid recoveries of 54% to 70%. The disadvantages of the solvent extraction technique are possible safety considerations related to the use of organic extractants. Also, few solvents are completely selective for only one solute; so the extracted fraction of the product also contains part of the impurity load.

While phosphoric acid can be purified by the other methods considered in our study, these processes are not favorable candidates for the following reasons:

- Alcohol precipitation needs a high degree of process control to precipitate the impurities without forming an excessive filter cake.
- Neutralization results in separated liquids that contain too much residual impurity.

- Dilution requires too much water for adequate dilution of the acid to precipitate part of the impurities as hydroxides.
- Sulfide precipitation showed only a minimal reduction in the iron content of the electrolyte and no reduction in the nickel content.
- Potassium and barium salts precipitation also showed little or no reduction in the metallic content of the electrolyte.
- Distillation studies showed that extreme pressure and temperature conditions are required to effect an adequate separation of impurities from acid.
- Electrolysis can remove metallic impurities from phosphoric acid solutions; however, the high ratio of cathode surface to electrolyte volume needed for effective metal ion reduction and removal in a large-scale process becomes a problem.
- Membrane separation lacks sufficient research and development to make it effective.

Based on the results of these studies, ion exchange has been selected for a scaled solution purification study and solvent extraction will continue to be assessed as a backup for the ion exchange process.

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PROCESSING OF WASTE SOLUTIONS FROM ELECTROCHEMICAL DECONTAMINATION

INTRODUCTION

The operation and eventual retirement of nuclear industry facilities will generate large quantities of surface-contaminated metallic waste. This waste, particularly that contaminated with transuranic elements, will require expensive handling, storage, and ultimate geologic disposal. The ability to remove surface contamination would eliminate both the expense of radioactive storage and disposal and the associated risk of environmental contamination. Decontamination contributes to conservation efforts through a recovery (and reuse) of irreplaceable alloying elements such as chromium and nickel--metals otherwise lost by burial.

Initial studies by Pacific Northwest Laboratory (PNL), in cooperation with Rockwell Hanford Company and UNC Nuclear Industries, Inc., have shown that electropolishing is a rapid and effective technique for removing plutonium and other radionuclide contamination from a variety of metal surfaces. As part of the nuclear waste management program activities sponsored by the Department of Energy, PNL is developing electropolishing into a large-scale decontamination technique capable of processing large volumes of surface-contaminated metallic waste.⁽¹⁾

Inherent in this electrochemical effort to reduce the volume of contaminated metallic waste is the production of secondary waste in the form of contaminated electrolytes. Consequently, solution treatment procedures are being developed to extend electrolyte life and minimize secondary waste volume.

Electrochemical decontamination requires a solution (electrolyte) that is stable at high current densities, tolerant of high metal ion, or salt, concentration without excessive sludging, and viscous enough to aid surface removal of contamination. A 75 wt% phosphoric acid solution meets these requirements and has been selected as the reference electrolyte for these decontamination studies.

Preliminary experiments on the decontamination of stainless steel using phosphoric acid electrolyte indicate that the solution should either be disposed of or cleaned when the stainless steel (Fe, Cr, Ni) content reaches about 6 wt% or the plutonium content reaches 150 mg/l. For direct disposal the electrolyte must be neutralized and converted to a solid.^(a) Calculations and tests (see Appendix A) show that this increases the volume. Although this is reasonable for disposal of secondary decontamination wastes from exposure reduction applications, it is not acceptable for treatment of transuranic wastes, where the objective is to minimize the volume of waste requiring geologic disposal. Therefore, there is a need to develop methods to remove impurities and extend electrolyte life by a factor of 5 to 10.

This report describes some of the solution purification alternatives that may be applied to the decontamination program. These alternatives include

- ion exchange
- solvent extraction
- precipitation
 - alcohol precipitation
 - neutralization
 - dilution
 - sulfide precipitation
 - potassium or barium salt precipitation
- distillation
- electrolysis
- membrane separation

Each of these potential processing methods is briefly discussed in terms of information from the technical and patent literature and our initial experimental evaluations. From these alternatives, two of the more promising solution purification techniques, ion exchange and solvent extraction, were selected for further study. The criteria involved in this evaluation process were safety, separation efficiency, remote handling, process scaleup, and ultimate waste disposal.

(a) There are currently no solution storage options for the aqueous spent electrolyte. Solidification, containment and either surface storage or burial is planned for the liquid wastes from electrochemical decontamination.

STRONG ACID ADSORPTION BY ION EXCHANGE

The removal of cationic impurities from concentrated phosphoric acid by conventional ion exchange generally is not considered a practical large-scale operation method. The necessary dilution of the 12 M acid and, in our case, the high-cation content of the impure acid makes a purification scheme by ion exchange extremely difficult. There are, however, examples in the literature where strong acid cation exchangers have been used in the purification of wet-process phosphoric acid.⁽²⁾ There are also citations describing phosphoric acid purification by the adsorption of the acid on ion exchange resins.⁽³⁻⁵⁾

PURIFICATION OF ALUMINUM FINISHING PHOSPHORIC ACID WASTES

Lancy Laboratories^(3,4) has developed and tested a continuous counter-current, ion exchange loop system for recovering phosphoric acid from aluminum finishing wastes. Their 23-ft-high, 2-in.-diameter column filled with a commercially available ion exchange resin reportedly processes 70 gal/day of approximately 32 wt% acid. The process recovers about 75% of the feed as 28 wt% acid with a 90% decrease in the Al content compared to the feed acid.

Unlike the acid-impurity separation by conventional ion exchange, the separation developed by Lancy Laboratories is based on strong "acid retardation."^(6,7) This observed phenomenon is a preferential adsorption of the acid molecule on an ion exchange resin. The acid salts (impurities) pass through the column leaving a pure concentrated acid on the resin. The adsorbed acid can be eluted by a water wash that allows the resin to be readied for the next loading without a separate regeneration step.

An acid purification unit (APU) developed by an industrial firm also relies on the adsorption of free acid on an ion exchange resin: the impurities pass through the bed with the acid held by the resin. The acid is eluted by a water wash.⁽⁵⁾ High acid recovery and efficient impurity removal are claimed for the APU, because of a short resin bed and rapid load/elution cycle. As one example of the operation of the APU, a 70% recovery of phosphoric acid from an aluminum finishing waste with about a 90% decrease in the Al content is

reported.⁽⁸⁾ However, it is pointed out that the system variables can be changed to emphasize product recovery or product purity.^(a) Figure 1 illustrates the process flow for spent acid purification.

FIGURE 1. Spent Electrolyte Purification by Reciprocating Acid Adsorption

PURIFICATION OF SYNTHETIC SPENT-ACID ELECTROLYTE BY RESIN ADSORPTION

The ease of operation and inherent safety of an APU are desirable features for our decontamination facility. However, our concentrated acid solutions with the anticipated high metal content as feed in our spent acid recovery system might be a problem in the direct application of the APU. To assess the unit's operation, we purified a small volume of our synthetic spent acid solution in an APU. The feed acid was prepared by electrolytically dissolving 304 stainless steel in 75 wt% phosphoric acid to give a solution containing

(a) C. Brown, ECO-TEC Limited, Toronto, Canada, personal communication, September 1977.

3.27 wt% metal ions. The synthetic solution's specific gravity was 1.60 g/ml; the viscosity was 20 to 30 centipoise; and the principal impurities (determined by x-ray fluorescence spectroscopy) were Fe = 34.4 g/l, Cr = 9.0 g/l and Ni = 5.0 g/l. This solution was processed in an APU at full strength through a small-diameter adsorption column. The operating parameters of the system were adjusted to emphasize a concentrated acid recovery.

The results of the test indicated that the full-strength spent acid could be processed at a scaled flow rate of 37 gal/hr with about a 40% reduction in the impurity load. The recovered acid was concentrated phosphoric acid. Diluting the product to 75 wt% gave a 90% acid recovery.

As the cation impurity content increases in phosphoric acid, the viscosity of the solution also increases.⁽⁹⁾ One of the problems noted in the above test was a lower than expected flow rate through the column due to a high feed-solution viscosity. Even with this potential processing problem, the purification of spent phosphoric acid by reciprocating ion exchange appears to be a suitable method for purification of electrochemical electrolytes.

SOLVENT EXTRACTION

The separation of impurities from phosphoric acid by solvent (liquid-liquid) extraction generally takes advantage of the solubility of the acid in a water-immiscible organic solvent. Because of the distribution criteria in liquid-liquid extraction, i.e., effective separation of a chemical specie is determined by its partition between the organic and aqueous phase according to the solubility (activity) of the specie in each phase, solvent extraction can be made specific to one substance rather than to a group of substances. In any acid processing method for removal of relatively high metal ion and radionuclide concentrations, we would want to extract a major fraction of relatively pure phosphoric acid into an organic phase, leaving most of the impurities in an aqueous phase. This general approach has been adopted in the purification of wet-process phosphoric acids where, over the past twenty years, numerous liquid-liquid extraction inventions have been reported. The following discussion has been taken from several reviews on wet-process acid purification and, where appropriate, from the patent literature.

SOLVENT EXTRACTION METHOD

Figure 2 illustrates a basic flow chart for the solvent extraction method, a flow that is essentially independent of solvent type. A water-immiscible or partially miscible solvent extracts the major portion of the product from an impure aqueous feed. The amount removed in a single extraction stage depends on a distribution coefficient. For phosphoric acid, the coefficient is defined by $D = P_2O_5 \text{ (organic)} / P_2O_5 \text{ (aqueous)}$. Since very few solvents are completely selective for only one solute, the extracted fraction of the product will also contain part of the impurity load. Following separation of the extract (generally the organic phase) from the raffinate (the aqueous waste), the product can be further purified by scrubbing the extract with a stream of previously purified product. The scrub will remove additional impurities that are carried into the organic phase. However, extra scrub steps will generally assess a penalty in product yield.

FIGURE 2. Typical Solution Flows in Solvent Extraction

Extraction and, if necessary, scrubbing separates the purified product from the aqueous feed. Recovery of the product occurs in a stripping stage where, in the case of phosphoric acid recovery, water is generally used to reclaim the product. Additional stripping operations can be used to improve product recovery. Most liquid-liquid extraction methods use a recycle of the extractant, scrub and strip solutions. The only major loss is the waste or raffinate.

There are basically three ways to effect large volume extractions: (1) a mixer-settler design that is a countercurrent flow device where there is mechanical mixing of the aqueous and organic feeds and a separation of phases by gravity (settling); (2) pulse columns that are vertical countercurrent devices where a pulse provides intimate mixing of the two phases; and, (3) centrifugal contactors that are concentric staged contacting devices where both mixing and settling are accelerated by a centrifugal force. The first method

for liquid contacting, a mixer-settler, is widely used in the minerals processing industry. The other two devices are used in the nuclear industry. Browne and Geier⁽¹⁰⁾ have recently reviewed and evaluated solvent extraction equipment.

PURIFICATION OF PHOSPHORIC ACID

Solvent extraction methods used to purify wet-process phosphoric acid can be broadly grouped into two classes: (1) solvent-acid systems where the distribution coefficient is reasonably constant to a low P_2O_5 concentration; and (2) solvent-acid systems where the distribution coefficient is P_2O_5 concentration dependent. The first class of solvents shows an increased extraction yield with multiple extraction stages; the second group shows little, if any, improvement in yield after a single extraction stage. The concentration-dependent solvents therefore have an advantage in a simplified extraction operation, but a disadvantage in the range of acid concentrations needed for economic extraction. The extraction range is normally between 20 and 70 wt% phosphoric acid.

Typical solvents considered concentration independent (Class 1) and prominently mentioned in the literature include

- four or more carbon alcohols, e.g., n-butylalcohol,⁽¹¹⁻¹⁴⁾ iso-amyl alcohol^(11,14)
- esters, e.g., butyl acetate^(13,15)
- alkyl phosphates, e.g., tri-n-butyl phosphate^(13,14,16)
- amines.⁽¹⁷⁾

Concentration-dependent solvents (Class 2) include

- four or more carbon ethers, e.g., iso-propyl ether^(12,13,18)
- esters⁽¹³⁾
- glycol ethers⁽¹⁸⁾
- ketones, e.g., methyl isobutyl ketone.^(12,13,18)

A British firm⁽¹⁹⁾ used methyl isobutyl ketone (MIBK) to extract and purify phosphoric acid in an industrial pilot study. In their study, the organic to impure acid volume ratio was 1:1 to 1.5:1. The normal operating temperature in their mixer-settler units was about 40°C. No purification limits nor acid yields were given in the reference, although the pilot plant was processing about one ton of acid per day. Improvements in the extraction system have since been covered under patents describing modifications (chemical additions) to the MIBK solvent.⁽²⁰⁾

In another industrial application, Israel's IMI-Institute for Research and Development used isopropyl ether (a Class 2 solvent) and then later used an improved ether/alcohol modified solvent (combined Class 1 and 2 solvents) to purify wet-process phosphoric acid. Mixer-settler studies⁽²¹⁾ using the ether solvent showed that an impure acid feed (about 74 wt% phosphoric acid, 9600 ppm Fe and 3300 ppm Al) could be purified in a single stage to give a 70 wt% phosphoric acid product containing 370 ppm Fe and 46 ppm Al. The purified acid yield was about 60%. For the ether extractions, temperature was controlled between 5°C and 30°C. The extraction temperature apparently affects both impurity removal and purified acid yield. Recovery of the acid in this process is by water stripping the organic phase at or above 30°C.

The addition of a concentration-independent solvent, an alcohol, to the isopropyl ether gave a modified solvent that improved the acid yield and decreased the necessary high-feed-acid concentration from about 75% to about 60% phosphoric acid.⁽¹²⁾

The above examples show that the impurity load in a concentrated phosphoric acid can be effectively decreased by solvent extraction methods. They also point out that relatively simple single-stage extraction and recovery is practical on an industrial scale. The use of a particular solvent (or modification to that solvent) can also be tailored to the separation process depending on the penalties one will accept in product purity and recovery. Because our particular problem of spent phosphoric acid processing is similar to the cleaning of wet-process phosphoric acid, the solvent extraction method for acid purification could be a reasonable alternative to electrolyte disposal.

EXTRACTION OF SYNTHETIC SPENT PHOSPHORIC ACID WITH MIBK

The use of liquid-liquid extraction for purifying wet-process phosphoric acid has a large amount of patent literature documenting its versatility and effectiveness as an impurity separation method. To assess this technique on our spent electrolyte, a Class 2 solvent was used as an extractant. MIBK was chosen as the solvent for a series of single-stage extractions. Table 1 illustrates the equilibrium of phosphoric acid (as P_2O_5) between the aqueous and organic phase and Table 2 shows the effectiveness of MIBK in purifying a wet-process acid. Data of this type provide a basis for comparison of our extraction results. An additional advantage of using this particular ketone is that information about the extraction of plutonium (a principal radioactive impurity), using MIBK as the solvent, is available from the reprocessing of nuclear fuels.⁽²²⁾

Several extractions were conducted on synthetic spent phosphoric acid solutions containing from 2 to 5 wt% metal ions (Fe, Cr, Ni) and from 0 to 1 g/l plutonium. The plutonium impurity was introduced as an oxide or as a metallic ion electrolytically dissolved in 75 wt% phosphoric acid. The Fe, Cr and Ni impurities were introduced into the acid by electrolytic dissolution of 304 stainless steel.

The liquid-liquid extraction procedure is illustrated in the flow diagram shown in Figure 3. All extractions and back extractions were made at ambient temperature in 250 ml separatory funnels. Samples of the feed, raffinate, extract, purified acid and/or reconstituted purified acid were analyzed by x-ray fluorescence spectroscopy. The analysis is described in Appendix B.

TABLE 1. Equilibrium Partition of Phosphoric Acid Between Water and Methyl Isobutyl Ketone at 40°C⁽¹²⁾

<u>Aqueous Phase</u> <u>Wt% P_2O_5</u>	<u>MIBK Phase,</u> <u>Wt% P_2O_5</u>	<u>Distribution,</u> <u>$\frac{P_2O_5(MIBK)}{P_2O_5(Aq)}$</u>
46	22	0.47
38	0.02	0.0005

TABLE 2. Distribution of P_2O_5 and Fe in Wet-Process Acid and MIBK at 23°C(12)

Wet Acid Feed, P_2O_5 /Fe, Wt	Residual Acid			Extract		
	% P_2O_5	%Fe	P_2O_5 /Fe, Wt	% P_2O_5	%Fe	P_2O_5 /Fe, Wt
90	45.8	1.3	35	25.0	0.1	250

FIGURE 3. Procedural Flow Diagram For Solvent Extraction

A summary of several individual extractions is listed in Table 3. Figure 4 is a diagram of one of the tests representing a possible process flow for the purification of a decontamination electrolyte.

In the second test (Table 3), about an order of magnitude decrease in the impurity level of the acid was found after processing. For this particular

FIGURE 4. Spent Electrolyte Purification by Solvent Extraction

test, the estimated recovery of acid from the feed was 60%. In tests 3-6, the decrease in the Fe, Cr, and Ni impurities was not as good as expected, since part of the impurity decrease was accounted for by dilution (makeup) with 75% H_3PO_4 to the original feed volume. Acid recoveries in these tests varied from 54% to 70%. The x-ray source necessary for plutonium analysis contributed higher background noise to the uncorrected Cr and Ni results shown in Table 3 and, therefore, resulted in a less reliable analysis. The results of these extractions show that the liquid-liquid method can be used for phosphoric acid purification. The important observation in these tests was the nearly total rejection of plutonium activity to the raffinate.

Thus, the literature from the wet process acid industry and the results from our own tests demonstrate that MIBK could be effectively used as an extractant for phosphoric acid. The major disadvantage of liquid-liquid

TABLE 3. Summary of H₃PO₄ Extractions Using MIBK

Test No.	Acid Feed Impurities, g/l				Raffinate, g/l				Purified Acid, (a) g/l			
	Fe	Cr	Ni	Pu	Fe	Cr	Ni	Pu	Fe	Cr	Ni	Pu
1	23.4	5.8	2.9	0	43.8	10.8	6.0	0	16	4	2	0
2	54.0	13.3	6.7	0	74.8	17.9	8.8	0	5	2	1	0
3	22.3	5.5	2.7	0.2 ^(b)	30.6	6.7	3.3	0.3	7	5	1	trace
4	19.0	4.7	2.3	0.3 ^(c)	37.4	8.6	5.6	0.3	10	4	1	0 ^(d)
5	0	0	0	1.0 ^(e)	0	0	0	1.0	0	0	0	0 ^(d)
6	22.3	5.5	2.7	0.2 ^(b)	41.4	8.9	4.4	0.2	10	4	1	0 ^(d)

(a) These values are corrected impurity levels for the purified acid after extraction, reconcentration to ~75% H₃PO₄ and makeup to the original feed volume with impurity-free 75% H₃PO₄.

(b) Plutonium impurity from electropolished Pu metal.

(c) Combination of plutonium oxide and plutonium ion.

(d) X-ray fluorescence analysis for plutonium was verified by low-level radioactivity measurements.

(e) Plutonium impurity added as the oxide.

extractions is principally one relating to safety. The combination of radioactive materials and potentially inflammable solvents will require special design and operation considerations.

PRECIPITATION

The removal of impurities from solution by precipitation is a time-related process depending on such factors as impurity concentration, temperature, hydrogen ion activity, nature of the solvent or mixed solvents, and other ions in solution. One of the several different precipitation methods that was evaluated as a possible means of purifying the phosphoric acid electrolyte was alcohol precipitation.

ALCOHOL PRECIPITATION

Alcohol precipitation combines the action of a completely miscible solvent with an acid feed and the addition of alkaline metals or ammonia.^(7,8,23) The impurities in the phosphoric acid are precipitated from the solvent/feed solution as complex alkaline or ammonium phosphates. The solids are separated by settling or filtering, and the solvent is recovered from solution by distillation.

Purification of Wet-Process Phosphoric Acid

The alcohol precipitation method for purifying wet-process phosphoric acid has been developed and patented in both Germany⁽⁷⁾ and the United States.⁽⁸⁾ The German patent covers a process using iso-propanol as the solvent. In one citation,⁽¹⁶⁾ an impure 70 wt% H_3PO_4 containing 0.5 to 1 wt% impurity load was processed to give a product acid containing no detectable cations except 0.003 wt% Fe and 0.002 wt% Cr.⁽²³⁾ Another citation⁽²⁴⁾ reports on the purification of 73 wt% H_3PO_4 containing sulfate anion and cation impurities (0.36 wt% Al, 0.48 wt% Fe). Calcium and ammonium ions were added to the acid feed. Subsequent addition of propanol aided the precipitation of calcium sulfate and metal phosphates. The alcohol was recovered by distillation. The product acid, a 95% yield, contained 73 wt% H_3PO_4 with 0.002 wt% Al and 0.005 wt% Fe.

Methanol has also been used as the solvent in a similar process developed and patented by the Tennessee Valley Authority (TVA).⁽⁸⁾ The use of methanol is mainly a cost advantage: iso-propyl alcohol is the more expensive. Also,

iso-propanol does form a low-boiling azeotrope with water, thereby complicating the alcohol recovery and potential recycle. Figure 5 is a simplified illustration of the alcohol precipitation method.

The purification of the feed acid increases with increased methanol and/or ammonia concentrations, but penalties are assessed in the filtering step and, subsequently, in the acid yield. For TVA's optimum conditions (listed on Figure 5), the methanol precipitation method removes greater than 90% of the Fe, Al and F impurities with about a 90% yield in product acid.

FIGURE 5. Wet-Process Phosphoric Acid Purification by Alcohol Precipitation

ALCOHOL PRECIPITATION OF SYNTHETIC SPENT ACID ELECTROLYTE

McCullough, et al.,^(8,23) have described the removal of the Fe impurities from concentrated wet-process phosphoric acid by alcohol precipitation. In the

purification of our spent acid electrolyte, the principal impurities that must be separated are Fe, Cr, Ni and Pu. The separation of Fe, Cr and Ni by alcohol precipitation was assessed from small-scale tests using a 75% phosphoric acid containing 2 wt% metal ions (the Fe, Cr and Ni electrolytically dissolved from 304 stainless steel). The spent electrolyte was first ammoniated, and then either methanol or isopropanol was added to precipitate complex ammonium-impurity phosphates. Table 4 summarizes the purified acid recoveries and the impurity concentrations from these precipitation tests.

The waste product from the alcohol precipitation method is the precipitate. The alcohol is separated from the filtrate by distillation, leaving 'purified' acid. An analysis of the washed and dried filter cake indicates that:

- The precipitate is amorphous (i.e., no definite crystalline pattern as determined by x-ray diffraction).
- The precipitate is partially soluble in hot water and very soluble in ammonium citrate.
- The precipitate begins melting at $\sim 150^{\circ}\text{C}$.
- The precipitate bulk density is fairly low, averaging between 1 and 1.5 g/cm^3 .

The solids from this purification process could probably be packaged for disposal without additional treatment.

The results of the alcohol precipitation tests show that a decrease in the impurity load in the spent electrolyte can be obtained with a reasonably high recovery of the phosphoric acid. The disadvantage of the alcohol precipitation method is the chemistry control needed to precipitate impurities, but at the same time not form an excessive filter cake. If the alcohol to phosphoric acid ratio is too low, e.g., about 0.5, the impurities are not carried into the precipitate but pass along with a part of the ammonia into the filtrate. If the alcohol to P_2O_5 weight ratio is greater than 2 and the ammonia to P_2O_5 mole ratio is greater than 0.4, then a larger ammoniated slurry is formed with

TABLE 4. Summary of Alcohol Precipitation Tests Using Methanol and Isopropanol

Solution		Alcohol/P ₂ O ₅ , wt	NH ₃ /P ₂ O ₅ , mole	Est. Acid Recovery, %	Feed Acid Impurity,		Product Acid Impurity,	
Rel. Vol.	Component				g/l		g/l ^(a)	
100	75% H ₃ PO ₄	0.5	0.13	78	Fe	25.3	Fe	19.7
6.3	NH ₄ OH				Cr	7.2	Cr	5.6
50	isopropanol				Ni	3.8	Ni	3.0
100	75% H ₃ PO ₄	3.4	0.38	90	Fe	25.3	Fe	14.5
16	NH ₄ OH				Cr	7.2	Cr	4.7
370	methanol				Ni	3.8	Ni	3.4
100	75% H ₃ PO ₄	1.9	0.40	79	Fe	25.3	Fe	3.1
17	NH ₄ OH				Cr	7.2	Cr	0.9
200	isopropanol				Ni	3.8	Ni	1.7
100	75% H ₃ PO ₄	3.0	0.28	80	Fe	25.8	Fe	15.4
12	NH ₄ OH				Cr	7.2	Cr	4.7
225	methanol				Ni	3.8	Ni	2.8

(a) The analysis of the purified phosphoric acid has been corrected to the corresponding feed acid volumes

corresponding difficulty in separating the solids and liquids, i.e., filtering. The optimum concentrations of alcohol and ammonia are described in McCullough's patent⁽⁸⁾ and related paper.⁽²³⁾

In alcohol precipitation, the principal solids are complex ammonium-iron phosphates and ammonium-hydrogen-phosphates. Because the Fe, Cr, and Ni concentrations were decreased compared to the feed, due to precipitation or coprecipitation, one may expect that a part of the plutonium impurity, in either ionic or colloidal form, would also be removed with the filter cake. Purification of a plutonium-contaminated electrolyte by the alcohol precipitation method has not yet been tested in our laboratory.

NEUTRALIZATION

The process of neutralization directly alters solution pH and can be considered a special case of precipitation separations. Separation of impurities from solution then depends on the addition of a neutralizing agent (acid, base, or water) to change the solution chemistry enough to precipitate the impurities.

McCullough⁽²⁵⁾ reports on a process where urea is added to wet-process acid to form a slurry. Nitric acid is then added to precipitate nitrates from the slurry to give a purified phosphoric acid solution.

Ammoniation of wet-process acid is another neutralization method for purifying phosphoric acids. Precipitation of complex ammonium-iron and/or aluminum phosphates has occurred at pH values from 1.5 to 3 during the neutralization of concentrated phosphoric acid with ammonia.⁽²⁶⁾

Tests were conducted to evaluate the effectiveness of neutralization techniques in removing 2 wt% metal impurities (Fe, Cr, and/or Ni) from 75 wt% phosphoric acid. Sodium hydroxide or ammonium hydroxide was added to a volume of the spent electrolyte to neutralize the solution of a pH of 3 causing the precipitation of iron. Adding 4 volumes of 12N sodium hydroxide to 5 volumes of the impure acid resulted in the precipitation of a thick gel. The pH of the colloidal solution was 2.2, and the precipitate was difficult to separate from the solution by filtration.

When the spent acid solution was neutralized with 14N ammonium hydroxide, precipitation began at a pH of about 1.8. Continued addition of the base to a pH of 3 resulted in nearly complete solidification of the partially neutralized acid solution. In both cases of neutralization, the heats of reaction helped to concentrate the solution by the evolution of water vapor.

During the partial neutralization of the metallic ion-loaded phosphoric acid with the sodium base, the sodium cation should remain in solution and the Fe, Cr, or Ni should precipitate as hydroxides. With ammonia or the ammonium base, however, the expected precipitate is first a complex ammonium-iron-phosphate (pH about 1.5) and then, with further neutralization, the precipitate is ammonium-hydrogen-phosphate (pH about 3).

We observed that, in each of the neutralization tests, the precipitates that formed in the concentrated acid/base or acid/ammonia mixtures were difficult to separate and to characterize. The separated liquid generally contained too much residual impurity for partial neutralization to be an effective method for the purification of a spent phosphoric acid electrolyte.

DILUTION

Dilution was another method evaluated as a way to remove metal impurities (Fe, Cr, and/or Ni) from 75% phosphoric acid. Water was incrementally added to a volume of the spent electrolyte to sufficiently change the solution pH to a value where precipitation of metallic ions as metal hydroxides (or phosphates) would occur.

About 100 volumes of water to 1 volume of spent electrolyte was necessary to cause the first sign of precipitation. At this point, the acid solution was neutralized to a pH of about 2.7.

Separations of the iron and chromium precipitates from the diluted acid solution by filtration followed by reconcentration of the filtrate back to a 75 wt% acid is one way the spent electrolyte could be processed. However, the volume of water needed for adequate dilution of the acid to cause precipitation of a part of the impurities seems to make this an impractical separations method.

SULFIDE PRECIPITATION

Studies were also conducted to evaluate the sulfide precipitation of metal ions from spent phosphoric acid electrolyte. Hydrogen sulfide gas was bubbled through a 75 wt% acid plus 2 wt% impurity solution to remove Fe and Ni by the precipitation of their sulfides. Calculations based on the solubility product of both iron and nickel sulfides show that these metallic ion impurities should precipitate from solution if the pH is suitably adjusted (Table 5).

A series of tests was conducted where the pH of the phosphoric acid solution was adjusted from 0 to 2.5 and then hydrogen sulfide gas bubbled through the partially neutralized solution for time periods of 1 to 8 hr. Analysis of the sulfide-treated solutions showed no reduction in the Ni content and only minimal reduction in the Fe content of the spent acid solution. The precipitates that did form were copper sulfides. Copper was introduced into the acid from electrical contacts during the electrochemical dissolution of 304 stainless steel into the phosphoric acid. Removal of copper from spent electrolyte is important since the erosion of copper current contacts often introduces this ion into the electrolyte. Some waste treatment systems cannot accept a liquid waste containing copper ion.

TABLE 5. Equilibrium of a Metal Sulfide in Solutions Containing Hydrogen Sulfide

pH	[H ⁺]	Ni ⁺⁺ , g/l	Fe ⁺⁺ , g/l	Precipitation	
				NiS ^(a)	FeS ^(b)
0	1	7×10^{-3}	2×10^6	yes	no
1	10^{-1}	7×10^{-5}	2×10^4	yes	no
2	10^{-2}	7×10^7	2×10^2	yes	no
2.5	3.2×10^{-3}	7×10^{-8}	20.7	yes	no
3	10^{-3}	7×10^{-9}	2	yes	yes
4	10^{-4}	7×10^{-11}	0.02	yes	yes

(a) Solubility product for NiS = 1×10^{-25}

(b) Solubility product for FeS = 3×10^{-17}

Note: The Fe and Ni content in 75 wt% H₃PO₄ containing 2 wt% metallic ions is 23 g/l and 3 g/l, respectively.

POTASSIUM AND BARIUM SALT PRECIPITATION

The removal of impurities from spent electrolyte by the addition of potassium salts with subsequent precipitation of a complex potassium-iron-phosphate was investigated. Adding about 2 wt% potassium carbonate to the 75 wt% acid plus 2 wt% impurity resulted in a precipitate that slowly developed over a period of 4 hr. Analysis of the filtrate showed an approximate 30% decrease in the Fe content, but no decrease in either Cr or Ni. This result coincided with that of Gilbert⁽²⁷⁾ in his patent on the clarification of phosphoric acids using potassium salts.

The precipitation of barium sulfate with coprecipitation of the impurities was also tested on the spent electrolyte. Sulfuric acid was first added to a volume of the impure phosphoric acid electrolyte. Barium carbonate was then added to precipitate barium sulfate. X-ray fluorescent analysis of the recovered filtrate showed only about a 3% decrease in the iron content and no change in either Ni or Cr content.

DISTILLATION

The separation methods described so far have in common a present commercial application for the purification of wet-process phosphoric acid or the purification of metal-finishing waste acids. Distillation is one of several other possible methods that can be used for specific impurity removal from a concentrated phosphoric acid.

Purification of a liquid by distillation normally depends on differences in the respective volatility of the solution components. The more volatile specie separates first and the least volatile component remains behind in the distillation boiler. In complex mixtures, the temperature or pressure can be controlled to separate one or more components of the mixture--a process of fractionation. In some complex mixtures, two components may distill at a constant temperature within a specific composition range, i.e., azeotropic distillation. However, even with the degree of freedom one has with distillation processes, the separation of a mixture of salts is generally not done because of the extreme pressure and temperature conditions required to effect separation.

Figure 6 shows the temperature-composition curve for phosphoric acid. At the lower temperatures, less than 300°C, water is removed (volatilized) from the acid, giving a more concentrated acid in the distillation boiler. Above an acid concentration of about 75 wt% phosphorus pentoxide (about 103 wt% phosphoric acid), the distilled vapor is mildly acidic. The problems in the separation of metallic impurities (salts) from phosphoric acid are apparent because of the extreme temperature conditions illustrated in Figure 6.

During our laboratory studies, we attempted to concentrate a synthetic spent electrolyte by distillation. As the volume of spent acid was reduced through the vaporization of water, the viscosity of the impure acid in the boiler increased to a point where the solution was no more than a gelatinous mass. Analysis of the residue suggested that the acid was concentrated to about 100% phosphoric acid. This residue was considered to be a mixture of pyrophosphoric acids and high molecular weight acid polymers. The volume reduction of the spent acid electrolyte by distillation amounted to only 12%.

FIGURE 6. Temperature-Composition Diagram for Phosphoric Acid
 Source: J. R. Van Wazer, Phosphorus and Its Compounds,
 Vol. 1, p. 774, Interscience Publishers, New York, NY,
 1958.

ELECTROLYSIS

Metallic impurities can be removed from phosphoric acid solutions at the cathode of an electrochemical cell, provided the reduction of the metallic ion is favored over the reduction of the hydrogen ion. Pourbaix diagrams, thermodynamic potential - pH diagrams, provide some information about the electrochemistry of metal ions in solution. The very simplified diagrams for iron and plutonium shown in Figure 7 define regions for the stability of ions in water at 25°C. The dashed line in the figure represents hydrogen reduction at the cathode. If mercury is used as a cathode, the potential for liberation of hydrogen is depressed by about 0.8 volt. This means that other ions in solution may be reduced at the mercury cathode, e.g., iron as shown in Figure 7a. However, even with a high cathodic potential, plutonium would not be reduced (Figure 7b).

The mercury cathode has found wide application in the analytical chemistry laboratory for separations and/or purification. Maxwell and Graham⁽²⁸⁾ have reviewed the essential parameters for using the mercury cathode and, also, some of its applications. Castro⁽²⁹⁾ describes mercury cathode electrolysis development in support of the Manhattan Project chemistry studies. For example, the optimum electrolysis conditions to remove iron and chromium from a uranium acid solution were 5 A current, less than 1 N acid solution, 50 ml electrolyte volume, 21 cm² cathode surface area, and a platinum anode.

These conditions demonstrate one problem with the mercury cathode method when applied to a larger than laboratory-scale process--namely, the ratio of cathode surface area to electrolyte volume needed for effective metal ion reduction. In our particular application, we have an additional problem in that any mercury in contact with the plutonium-contaminated solutions will be considered radioactively contaminated. Special handling in the secondary processing of the iron, chromium, and nickel from the contaminated mercury will also be required.

FIGURE 7. Pourbaix Diagrams for Iron(a) and Plutonium(b)
 Source: M. J. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, pp. 210, 313, Pergamon Press, New York, NY.

The factors generally considered to govern the efficiency of the mercury cathode method include

- nature and concentration of the acid. Sulfuric acid is the most commonly used and studied electrolyte, although phosphoric acid has been used in methods for the removal of iron. The acid concentrations are adjusted to prevent precipitation. For example, iron can precipitate as the hydroxide at a pH of 3. The efficiency of metal ion reduction generally decreases in the more concentrated acid.
- amount of mercury. The amount of mercury generally depends upon the specific separation desired. In one study,⁽²⁸⁾ the removal of iron was observed to be inversely proportional to the mercury surface. The lower limit for the amount of mercury is dictated by the impurity loading, that is, the amount of mercury impurity metal amalgam.
- agitation. A continuously fresh mercury surface maintains a high cell efficiency. As the mercury surface or pool becomes loaded with iron, copper, or other metals, the overvoltage for hydrogen gas formation becomes less negative thus decreasing the separation efficiency.
- time. For small volume separations, the electrolysis time can vary from 10 to 15 min up to several hours.
- current density. The current density (A/cm^2 cathode area) affects both electrolysis time and electrolyte temperature. The applied current is usually set as high as practicable without excessive boiling of the electrolyte.

Iron and nickel have been removed from a synthetic spent acid electrolyte (2 wt% iron, chromium, and nickel in 75 wt% phosphoric acid) by the mercury cathode method. In one test, the time for 90% removal of the iron and nickel was about 24 hr for the following conditions: cathodic current density of $0.2 A/cm^2$, 350 ml electrolyte volume, and 40 ml mercury volume. As expected, the chromium ion in solution was not reduced on the mercury cathode.

A second electrolysis experiment conducted at a lower current density, 0.1 A/cm^2 , gave essentially similar results to the above test. In this experiment, nickel was separated at a constant rate of about 5%/hr and iron was removed from the spent electrolyte at a rate of 2.5%/hr over a 4-hr period. Again, there was no decrease in the chromium content of the spent acid electrolyte.

MEMBRANE SEPARATION

Another method for separation of impurities from an aqueous media takes advantage of semipermeable, ion-selective membranes. These separation processes depend on the permeation of the membrane by some of the chemical species in contact with it. Typical membrane processes include

- Dialysis - both cation and anion diffusion from a colloid or waste solution to a "pure" water side of an ion-permeable membrane
- Reverse osmosis - pressure-assisted diffusion of water from waste side of a membrane to the "pure" water side
- Donnan dialysis - application of a cation exchange membrane to effect separation of metal ions from a salt solution to an acid solution
- Electrodialysis - electrolytic-assisted separation of cations through a cation permeable membrane and anions through an anion-permeable membrane.

Donnan dialysis has the potential for continuous processing of waste streams where, for example, Cu, Ni, Cd, or Cr are recovered from electroplating wastes.^(30,31) This method may be applicable to the purification of the waste decontamination electrolyte, although this method has not been fully assessed, either through literature or experimental evaluation.

An evaluation of the applicability of membrane technology for purification of spent phosphoric acid electrolyte was conducted by program consultants from the Hydrite Chemical Company. The following problems were noted: 1) the relevant processes are not developed industrially; 2) high viscosity reduces mobility, throughput rates and efficiency; and 3) the high acid concentration and complexing characteristics of the phosphate ion result in an unfavorable equilibrium situation. It is concluded that membrane technology would not be applicable without a major research effort.

PRELIMINARY EVALUATION OF ACID PROCESSING METHODS FOR THE DECONTAMINATION ELECTROLYTES

Any method used in processing a spent decontamination electrolyte will generate a certain volume of secondary waste. However, this volume of secondary waste should be considerably less than the volume of spent electrolyte in order to reduce the volume of solutions requiring final disposal. Criteria useful in evaluating possible methods of solution processing include safety, effectiveness, and economics. In this preliminary study, economics is less important than safety and effectiveness. Another major consideration is to find a method that is sufficiently developed to be transferred directly to the electrolyte purification study.

Based on the preceding discussion of the various possible separation methods, we can identify methods that would not be practical at this time. These methods include

- Distillation. This is not a promising method due to extreme temperature and pressure requirements for the separation of the acid values (P_2O_5) from the metal salt impurities. Distillation will, however, be used as part of any purification scheme as, for example, in acid concentration steps or in the separation of organics from an aqueous/organic solution.
- Electrolysis. For a large-scale process, the high ratio of cathode surface to electrolyte volume needed for effective metal ion reduction and removal becomes a problem. Also, special procedures would be required to purify the contaminated mercury for recycle.
- Membrane Separations. These are still in the development stage and may eventually prove to be practical.
- Precipitation and Neutralization. These methods have the inherent disadvantage of adding nonrecoverable materials to a processing scheme. Several patents covering wet-process acid purification show that these methods can be effective. However, the processing time required and the chemical additions suggest that these methods are not appropriate for contaminated electrolyte purification. Although alcohol precipitation is an

effective purification method, it is also a less acceptable method for this application because of the large volumes of alcohol required and the associated safety problems.

The above methods could with further development be applied to spent electrolyte purification. However, since one goal of this study is to transfer existing technology not requiring extensive process development, the solvent extraction and ion exchange methods appear more promising:

- Solvent Extraction. Solvent extraction has been applied in the wet-process phosphoric acid and fertilizer industries with favorable economics and effectiveness. Solvent extraction of the phosphoric acid from the spent electrolyte can be a flexible, easily controlled processing scheme. There are a number of solvents that can be used to optimize the purification and the recovery of the acid. One major drawback in solvent extraction is the use and recycle of flammable organics.
- Ion Exchange. The ion exchange method for spent electrolyte purification has been marketed recently as a "complete" unit for application in the metal finishing industry. The use of an industrial acid purification system has certain advantages over solvent extraction which include
 - 1) a commercially available, self-contained processing unit
 - 2) no chemical additions and/or extensive secondary solution recycle schemes
 - 3) operational flexibility in the "purified" acid product. It is possible with the acid purification unit to obtain a concentrated acid product, whereas with solvent extraction the water stripping step will always give a very dilute acid product.

Of these two more promising purification approaches for the separation of metallic and radioactive impurities from a phosphoric acid electrolyte, the ion exchange method used in the acid purification unit has been selected for a scaled solution purification study. A unit has been purchased and a detailed evaluation of its operation is underway.

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APPENDIX A

ANALYSIS OF SPENT ELECTROLYTE DISPOSAL BY NEUTRALIZATION AND SOLIDIFICATION

APPENDIX A

ANALYSIS OF SPENT ELECTROLYTE DISPOSAL BY NEUTRALIZATION AND SOLIDIFICATION

Laboratory-scale decontamination of stainless steel parts using phosphoric acid shows that the electrolyte should be either disposed of or cleaned when the dissolved metal (Fe, Cr, Ni) content in solution reaches about 6 wt% or when the plutonium concentration reaches 150 mg/l. Assuming a 0.001 in. surface removal from the steel, a metal density of 492 lb/ft³, and an electrolyte specific gravity of 10.4 lb/gal, a mass-volume calculation then shows that about 15 ft² of metal surface area per gallon of electrolyte can be decontaminated within the above limits.

In order to dispose of the spent electrolyte, the solution must be neutralized and then converted to a solid form. Neutralizing a low pH phosphoric acid to a pH of 3 or 4 will begin the precipitation of complex phosphates. The continued addition of a suitable basic material could lead to partial solidification of the aqueous spent electrolyte. During neutralization of the acid, the heat of reaction and the solidification process by the evaporation of some water.

One method to neutralize the spent acid is by the stoichiometric addition of magnesium oxide. The products of neutralization will be complex metal phosphates and a relatively insoluble magnesium hydrogen phosphate. For each gallon of electrolyte neutralized, about 4.2 lb of magnesium oxide must be added. To neutralize the spent acid with caustic (NaOH) to obtain the sodium hydrogen phosphate product, about 8.5 lb of caustic must be added to each gallon of electrolyte. Caustic addition has the disadvantage of a water-soluble product in addition to an increased volume of chemicals.

We can assume at this time that storage of the neutralized waste will be in 55-gal, polyethylene-lined, steel drums. The maximum allowed weight for storage of a low-level contaminated solid is 880 lb/drum. If the waste solid

has a bulk density equal to or less than 140 lb/ft^3 (the approximate density of the mineral newberyite, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), then each drum can be filled to about 73% of capacity to stay within the weight limit.

Neutralizing a given volume of spent electrolyte with magnesium oxide (and expelling most of the excess water) gives a solids volume for disposal nearly the same as the initial liquid waste volume. However, neutralizing with caustic increases the waste volume for disposal by about 30%.

Presently, we are solidifying the waste with excess sodium hydroxide. We find, in practice, that the waste volume increases even more than the 1.3 times suggested in the above analysis. Therefore, a reprocessing method that permits cleaning and reuse of the spent electrolyte would benefit the electrochemical decontamination program by reducing the waste volume as compared to the solidification methods suggested above.

APPENDIX B

ANALYSIS OF THE ELECTROCHEMICAL DECONTAMINATION ELECTROLYTE

APPENDIX B

ANALYSIS OF THE ELECTROCHEMICAL DECONTAMINATION ELECTROLYTES

X-ray energy spectrometry is used in the routine chemical analysis of the decontamination electrolyte. X-ray fluorescence is a relatively easy, fast technique for liquid sample analysis and requires little or no sample preparation compared to other analytical methods such as atomic adsorption spectroscopy (AAS).

The procedure followed for the bulk of the analysis of purified spent electrolyte was to place a 5 ml aliquot of the solution in a spectrocup having a 0.2-mil-thick Mylar[®] window. The counting time for the sample was 200 sec. An x-ray fluorescence system was used at 40 kV, 10 mA, with a Nb target and filter, and in an air atmosphere to determine the Fe, Cr, and Ni impurities in the 75 wt% H_3PO_4 solutions. Phosphorus and Fe were analyzed at 32.5 kV, 20 mA, with a Ti target, no filter, and in a He atmosphere. Plutonium was analyzed by x-ray fluorescence at 47.5 kV, 2 mA, with a Ba target and no filter, and in an air atmosphere. However, routine analysis for Pu will be by radioactive counting techniques rather than x-ray fluorescence.

Figure B.1 shows the nearly linear relationship between x-ray counts and Fe concentration in the 75 wt% H_3PO_4 solution matrix. The Fe, Cr, Ni, and P contents of standard solutions, prepared by electrochemically dissolving a known weight of 304 stainless steel in a volume of 75 wt% H_3PO_4 , were analyzed by AAS as a verification of the x-ray analyses. A National Bureau of Standards Fe sample provided the reference Fe concentration for the analysis and the Cr and Ni values were proportioned to the Fe value. These solutions were used to establish calibration curves for the x-ray analysis and to determine counting reliability.

The x-ray fluorescence counting reliability was assessed by repetitive counting of the same sample and by repetitive counting of different sample

volumes of the same solution. The sample analysis was found to be reliable to within $\pm 5\%$ at a 68% confidence level. Normal statistical precision based on the total counts obtained on our standard solutions suggests that the relative error should be within $\pm 3\%$ at a 68% confidence level.

FIGURE B.1. Relationship Between X-ray Counts and Iron Concentration in the 75 wt% Phosphoric Acid Solution Matrix

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