Recycling Zinc Phosphate Sludge

by Christopher J. Baldy

The cost of sludge disposal can contribute significantly to the cost of product manufacturing. An opportunity exists to eliminate this cost of land disposal of sludge resulting from the zinc phosphate pretreatment process. In addition, the cost of the phosphating process may be reduced by reclaiming this sludge to a zinc-phosphate replenishment solution and other useful products.

For those not familiar with phosphating processes, a one-to-one relationship exists between the amount of phosphate deposited on the metal substrate and the amount of sludge generated. For many automotive and industrial processes, this sludge consists of iron, zinc, manganese, nickel, phosphate, and oil. The products, which result from the recycling process, are oil, which may be used as a heating fuel; a zinc phosphate concentrate; and a cake of iron phosphate. If desired, this iron phosphate can be further processed to an iron phosphate concentrate and iron oxide, which may be used as a pigment for paint.

Several methods for reclaiming zinc containing sludge have been proposed previously. Certain companies offer reclamation services of zinc-bearing waste through a high-temperature metal recovery method; however, the relatively low level of zinc contained in this sludge makes this process of little cost benefit for zinc phosphate sludge. On the contrary, the recovery process described in this article provides a benefit to the product manufacturer who can use the zinc phosphate replenishment solution reclaimed from the zinc phosphate sludge.

U.S. Patent 5,376,342 was granted for a process very similar to the one described below; however, attempts to reproduce the patent examples resulted in a pH of 0.8, which is below the specified level of 1.5 to 2.5. If the amount of acid was reduced to achieve the minimum pH specified (pH 1.5), the sludge slurry became extremely thixotropic and unworkable. Additionally, no mention is made of the removal of the oil prior to digestion of the sludge. This is an essential step, as the oil is typically 20 to 25% by weight of the sludge, and total digestion of the sludge is not possible without first removing this oil component.

Additional patents have been issued for various other methods of reclaiming zinc phosphate sludge. U.S. Patents 4,986,977 and 3,653,875, and JP 03134181 discuss the recovery of products after an initial alkaline digestion. Patent EP 608874-A1 discusses the recovery of metals from such sludge using a strong acid cation exchange resin. U.S. Patent 5,273,667 discusses the conversion of the phosphate sludge to a lubricant additive. Finally, the U.S. National Technical Information Service, Public Bulletin # 211,933 (1972) describes a solvent extraction procedure for recovery of sodium phosphate, zinc, and iron. Each of these methods fails to discuss the removal of the oil present, and are of limited use for the production of products useful to the product manufacturer.

The specific technical aspects of the process to be described may be segregated into three phases. Phase I is the separation of oil from the sludge. Phase II is the extraction of zinc, manganese, and nickel from the sludge following digestion with phosphoric acid. Phase III is the conversion of the iron phosphate residue from Phase II to pigment-quality iron oxide, and sodium phosphate that may be acidified to an iron phosphate concentrate.

EXPERIMENTAL

The following testing was conducted on both sludge from a zinc-nickel phosphate process and from a zinc-nickel-manganese phosphate pretreatment process. Due to the hydrophilic nature of this sludge, typical sludge obtained from an automotive pretreatment process is only 40 to 55% solids. The presence of up to 25% by weight oil in this sludge poses a significant hindrance to the recovery process. Removal of the majority of the oil is essential to the full recovery of all useful components.

This removal of oil is accomplished by the addition of hydrogen peroxide to an acidic dispersion of the sludge that displaces oil from the remaining mixture. This clean separation becomes possible through the oxidation of certain components of the oil. Upon addition of hydrogen peroxide, the oxidation reaction is observable through the separation of the oil and the conversion of a portion of this oil to a tar. Upon completion of the oxidation reaction, the reaction vessel contains a white iron phosphate precipitate, a green metal phosphate concentrate above, and an oil layer that is floating on top. This oil that floats above the aqueous layer contains both liquid and a tar type of material. Multiple possibilities are available for removing the oil layer from the top of an aqueous solution. We used an oil skimmer for this operation.

The tar portion was then rinsed with xylene and analyzed along with the liquid oil by IR and 13C NMR. The IR and NMR spectra show the liquid to be a long-chain aliphatic oil with a small amount of unsaturation, essentially a mineral oil. The tar is a mixture of components. The major components are a long-chain fatty acid, a bisphenol A-type component, and silica. The full impact of this discovery is still not clear, but it is expected that this oil oxidation process will have several additional applications, possibly to include removal of oils from metal surfaces.

The solid white iron phosphate precipitate may be separated from the zinc, nickel, and manganese containing supernatant liquid using a filter press, or in our case, a vacuum filtration process. Depending upon the particular source of the sludge, it may be beneficial to have a magnetic collector that collects the iron fines present in the sludge, prior to dispensing the solid material to the filter press. Another point worth mentioning is that no hopeite or phosphophyllite or iron (III) phosphate crystals were found in this
solid material by X-ray diffraction analysis. Elpasolite (K₂NaAlF₆) was found as a minor crystalline species in both the zinc-nickel and zinc-nickel-manganese sludges. In the zinc-nickel sludge, Fe₇(PO₄)₆ was found in trace amounts. This verifies that the components of the sludge are amorphous in nature.

The optimized procedure for the recycling of zinc phosphate sludge (the specific phosphating line example is a zinc-nickel-manganese line) into usable components is described below. Also included are the representative yields. This process is represented schematically in Figure 1.

### Phase I

To 100 parts by weight sludge (50% solids), 400 parts 25% phosphoric acid are added. A one-hour digestion of the dispersion is conducted at 82°C. While at 82°C, 10 parts 30% H₂O₂ are added under slow stirring conditions. At the end of this addition, the dispersion is allowed to settle without stirring for 10 minutes. Using a skimmer, the 13 parts of oil released float above the dispersion and are collected.

### Phase II

To the remaining suspension is added 45 parts of 40% sodium hydroxide to raise the pH to 2.5 prior to filtering. The 200 parts (30% solids) of residue (iron phosphate) are saved for the third phase of the process. The 350 parts of filtrate collected contain 6 parts zinc, 1.8 parts manganese, 0.1 part nickel, and 90 parts phosphate. This is used in the formulation of a zinc phosphate concentrate.

### Phase III

The iron phosphate residue from the previous stage is placed in 400 parts water. To this suspension is added 200 parts 15% sodium hydroxide over 60 min at 23°C. This suspension is then heated to 82°C for 15 hours for good color development to a red-brown pigment. The pH is then reduced to about 7 by the addition of 17 parts 85% phosphoric acid. The suspension is allowed to settle for 10 minutes and then filtered hot.* The 25 parts Fe₂O₃ that result may be used as a pigment in paints. The 630 parts filtrate contains NaH₂PO₄, and may be acidified with 20 parts H₃PO₄ to provide an iron phosphate concentrate.

Summarizing the above processes, 100 parts 50% solids zinc-nickel-manganese phosphate sludge are digested in 400 parts 25% phosphoric acid and 10 parts 30% hydrogen peroxide added, which separate 13 parts oil. The supernatant liquor contains 6 parts zinc, 1.8 parts manganese, and 0.1 part nickel. The iron phosphate residue is further alkaline digested in 200 parts 15% sodium hydroxide to produce 25 parts Fe₂O₃ plus 650 parts of iron phosphate concentrate.

### CONCLUSION

The above-described reclamation process offers cost savings associated with reduced disposal costs, reduced replenishment costs, and possibly cash return from the generation of other useful components. This process is relatively simple, requiring minimal capital expenditure, and is minimally labor intensive. Finally, this process provides the opportunity for environmental stewardship through the complete recycling of all by-products of the phosphating process into useful materials as opposed to land-filling these materials as waste.

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*All filtering referred to in this process is by vacuum filtration using a Buchner funnel as opposed to a filter press.