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Waste Minimization Opportunities At An Electric Arc Furnace Steel Plant Producing Specialty Steels

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Waste reduction assessments have been carried out in the Armco, Inc. Butler, Pennsylvania electric arc furnace (EAF) specialty steelmaking complex. These assessments were intended to develop waste reduction options for two hazardous waste streams at this facility: heavy metals waste and corrosive waste. Waste reduction options considered were in one of two categories: source reduction or recycling (in the same order of preference). Treatment was considered only if waste reduction options were unavailable.

INTRODUCTION

Following the Congressional mandate on reduction of hazardous waste as expressed in the Hazardous Solid Waste Amendments of 1984 (HSWA), the EPA Office of Research and Development Hazardous Waste Engineering Research Laboratory (HWERL) during 1986 and 1987 offered various industrial facilities the opportunity to act as host sites at which specially selected group of engineering consultants (under EPA sponsorship) would assess the opportunities for reduction of selected hazardous wastes generated at these sites. One of the industrial facilities agreeing to act as a host site for a waste reduction assessment was the Armco Inc. Specialty Steel Division in Butler, Pennsylvania. Versar Inc. was selected by EPA to be the engineering consultant to perform the assessment. The results of the assessment conducted at the Armco facility are discussed in this paper.

In the course of performing the waste reduction assessments, the consultants involved were to apply and refine as appropriate a methodology developed for carrying out these assessments. The methodology as finally developed is described in detail in "The EPA Manual for Waste Minimization Opportunity Assessments" [*1*].

DEVELOPMENT OF WASTE REDUCTION OPPORTUNITIES

The primary emphasis in this waste reduction assessment was to develop and evaluate waste reduction opportunities for two principal hazardous wastes generated at the Armco Inc. facility: emission control dust and sludge from electric arc furnace (EAF) steelmaking operation; and waste pickle liquors and rinse waters from cleaning of the stainless and alloy steel strip products prior to shipment. This assessment was performed during the summer of 1986. The Versar assessment team included the assessment project manager (a senior chemical engineer with 37 years of process engineering and project management experience including approximately 13 years of environmental engineering experience), a senior physical chemist with 20 years of experience, and a steel industry consultant (a metallurgical engineer with 40 years of experience). The assessment focused on two plant areas that generate these wastes: the melt shop in the main plant where the EAF emission control waste is generated, and plant no. 2, which generates a hydrofluoric acid/nitric acid pickle liquor and rinsewater from cleaning of stainless steel strip prior to shipment. Other pickling facilities in the main plant generate a number of sulfuric acid, hydrofluoric acid, and nitric acid wastewater streams, but these wastes are presently comingled prior to wastewater treatment. Plant No. 2 generates a single segregated pickle liquor waste stream that appeared amenable to waste reduction possibilities. Each of the assessments performed at the two Armco facilities are described below.

Melt Shop Emission Control Sludge Waste Reduction Assessment

Based on the facility information received by the assessment team, process and waste handling operations at Armco's main plant were as follows. The main plant at Armco's facility consists of three electric arc furnaces (EAFs) in the melt shop that produce stainless and silicon steels, hot and cold rolling operations to fabricate steel strip and coil, six pickling lines for both stainless and silicon steels, and annealing facilities located in several buildings on a site covering about one square mile. Also located on the site are wastewater treatment facilities, the engineering services building, and a number of surface impoundments used for disposal of nonhazardous liquids and sludges generated primarily from on-site neutralization of spent pickling liquors and rinse waters. The facility produces several types of silicon steels as well as 300 and 400 series stainless steels. Since 1987, the facility also produces a significant quantity of low carbon mild steel. However, plant management is currently planning on returning to the stainless/alloy steel production regime.

Silicon and stainless steels (the latter made in 300 and 400 series) are produced by melting selected batches of scrap, fluxes (including fluorspar), and ferroalloy additives in the presence of oxygen in three-165 tons EAFs at

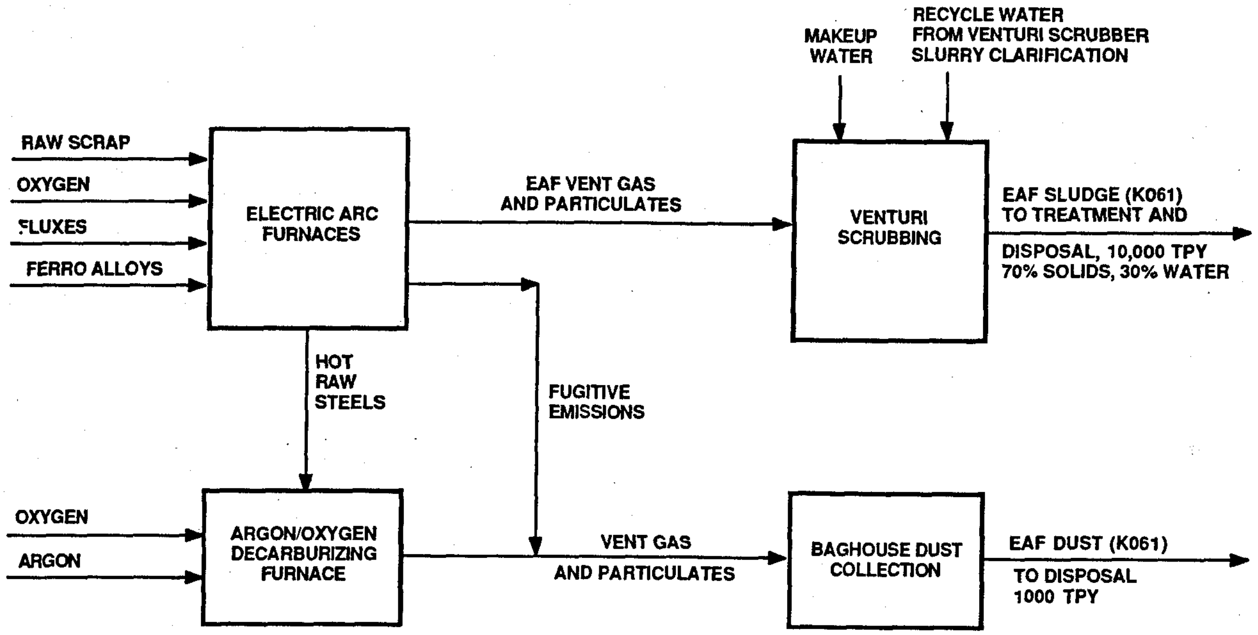

Figure 1. Simplified schematic of K061 waste generation and treatment at Melt Shop, Armco, Inc., Butler, PA.

the melt shop. Approximately 670,000 tons of EAF steels are produced annually at the Butler, facility. The three EAFs, together with an AOD furnace at the melt shop, generate vent gases containing about 8,000 tons per year (TPY) of particulate emissions. Of these emissions, approximately 7,000 TPY are removed from the EAF vent gases using venturi scrubbing; the remaining 1,000 TPY are recovered as EAF fugitive emissions as well as from AOD vent gases using a reverse-air baghouse. Figure 1 is a simplified schematic of the K061 waste generation and treatment processes.

Assessment Step

This phase of this waste reduction assessment began with a detailed inspection of the melt shop area by the Versar team. During this visit, the processes that generate and treat the K061 waste were carefully studied. The process flow was traced from the point of waste generation to the discharge of the treated K061 waste. A schematic illustrating the existing waste treatment procedure is shown in Figure 2.

The melt shop generates EAF emission control dust and sludge. Table 1 is the most recent metals analysis of the EAF venturi scrubber sludge available from the plant; the data shown were obtained in 1983. The venturi sludge represents about 90% of the K061 hazardous waste discharge from the plant. Also included in Table 1 is a recent Versar analysis (1987) of the baghouse dust representing AOD and fugitive emissions from the melt shop.

As shown in Figure 2, the present EAF dust treatment process consists of a water clarification system for the venturi scrubber slurry (the latter contains about 10,000 ppm solids as produced in the venturi scrubber) and a system for treating a blowdown stream of recycled water from the venturi scrubber slurry clarification step (about 10% of the venturi scrubber flow) for hexavalent chro-

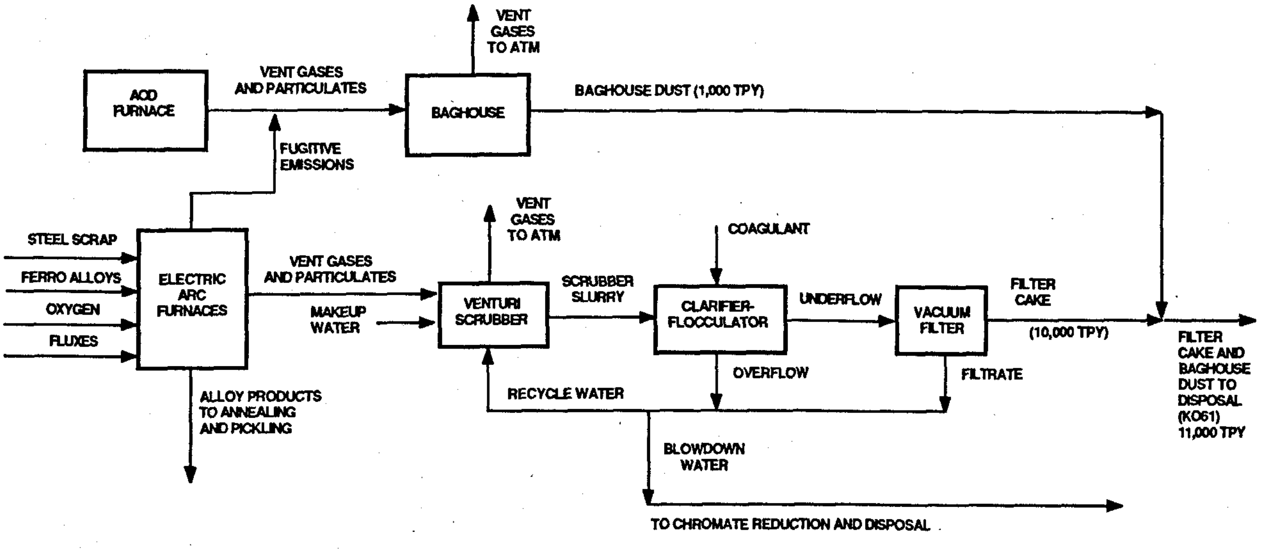

Figure 2. Simplified schematic of EAF dust treatment at the Armco Main Plant, Butler, PA.

TABLE 1. COMPOSITION OF ARMCO MELT SHOP EAF EMISSIONS CONTROL WASTE (K061).

Parameter	Amount present (weight percent, dry basis) Venturi sludge[a]	Baghouse dust[b]
Iron	39.9	27.6
Manganese	3.4	2.8
Silica (SiO_2)	4.9	—
Aluminum	0.3	0.3
Calcium	3.1	5.8
Chromium (total)	1.7	1.2
Copper	0.25	1.7
Nickel	0.36	0.69
Lead	3.1	0.73
Zinc	10.5	8.4
Magnesium	2.3	3.1
Cadmium	0.041	0.009
Barium	0.011	0.002

[a] Armco data (1983).
[b] Versar data (1987).

mium reduction (the latter system not shown). The clarifier underflow sludge from the water clarification system is filtered in a rotary vacuum filter. The filter cake is then combined with the baghouse dust collected from the decarburizing operation and melt shop fugitive emissions, and the total waste stream (11,000 TPY) classified as K061 is sent to offsite hazardous waste landfills. Armco's disposal cost is \$100/ton or approximately \$1,000,000 per year to dispose of the K061 waste.

Armco advised the assessment team that attempts had been made to recycle the K061 material to the EAFs as briquetted material. These attempts did not develop into a feasible technique because the bulk of the hazardous constituents in the dust, i.e., cadmium, chromium, and lead, were either revolatilized or swept into the vent gases and reappeared in the EAF vent gas emissions. Another mitigating factor against reclamation of this material is the relatively low zinc level (10 to 12%). In EAF operations producing primarily carbon steels, the zinc level of the emissions is usually much higher, i.e., in the 15 to 20 percent range due to the high percentage of galvanized steel scrap used in the feed to the furnaces. In order for EAF dust to be economically attractive to reclaimers, it should have at least 15 to 20% zinc and preferably in the 25 to 50% range.

Because of the nature of the scrap Armco purchases for use in the EAFs and the products manufactured, i.e., stainless steels, it is highly unlikely that levels of chromium, cadmium, and lead could be reduced to the point where the EAF dust would pass the TCLP test, Toxicity Characteristic Leaching Procedure, which has now largely replaced the EP-toxicity testing procedure, which means that this waste must continue to be as RCRA listed waste K061. Thus, source reduction and recycling/reuse were ruled out as viable waste reduction options for reducing or eliminating the K061 waste generated at this plant. The only other approach available would be to detoxify this waste in a technically and economically feasible manner so that it could be disposed of in a nonhazardous landfill as a delisted waste. This approach, while not waste reduction, at least offered Armco the possibility of disposing of the waste as a nonhazardous material.

The current Best Demonstrated Available Technology (BDAT) regulations recently promulgated (August 8, 1988) by EPA specify that K061 waste be chemically stabilized before disposal in a hazardous waste landfill. This regulation is currently undergoing a U.S. Court of Appeals review based on appeals by the steel producers. EAF steel producers can, if their K061 waste is rich enough in zinc, ship this waste to zinc reclaimers using a high temperature roasting process, i.e., Horsehead Resource Development, Palmerton, Pennsylvania.

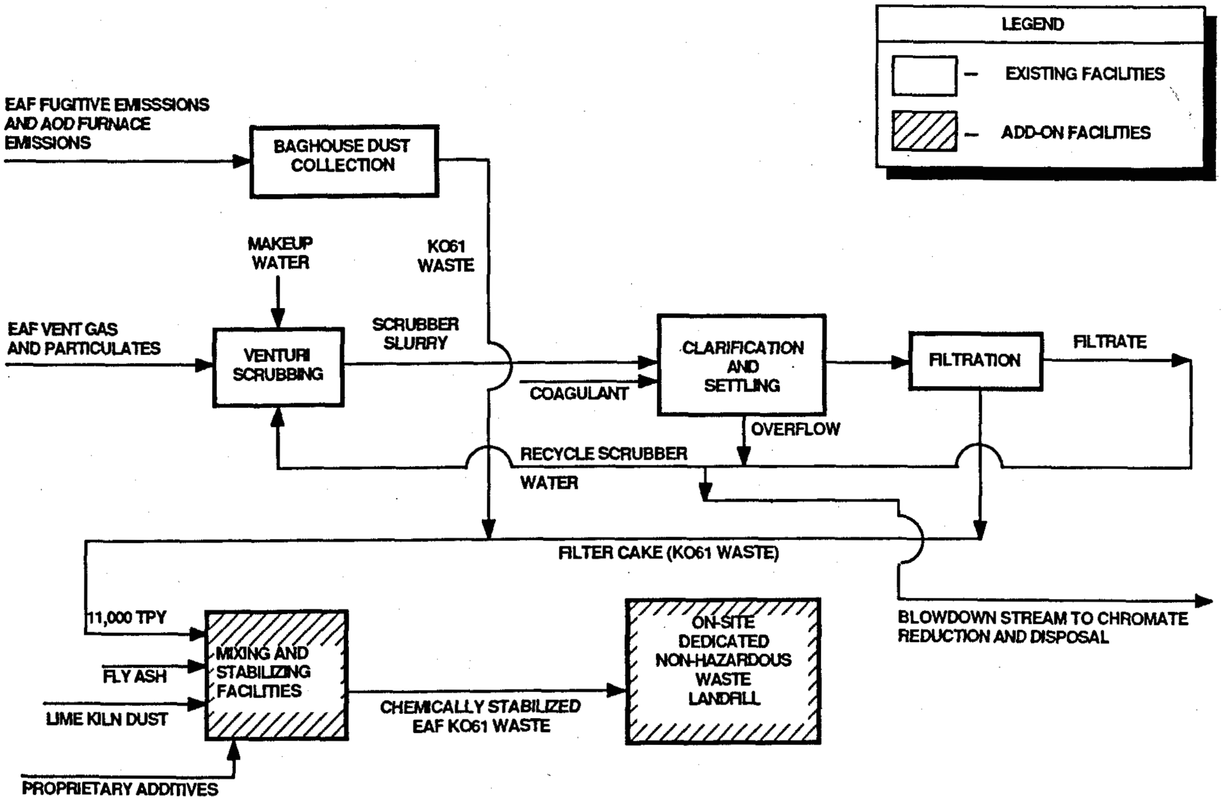

Figure 3. Simplified schematic of Versar-proposed modification of K061 waste treatment at Armco, Butler, PA., Main plant.

The assessment team proposed a detoxification option wherein the K061 waste is immobilized in an insoluble matrix using chemical stabilization of the combined venturi scrubber sludge filter cake/baghouse dust. Based on the pozzolanic reactions of materials containing anhydrous alumino-silicates (such as flyash), alone, or in combination with lime kiln dust and water, absorption and/or chemical stabilization of the heavy metals in the EAF dust would occur forming a calcium-alumino-silicate matrix, thereby rendering the quantities hazardous constituents in the dust essentially immobile. The use of small quantities of soluble silicates would tend to present leaching of chromium (the most leachable of the hazardous heavy metals present). Armco would need to perform laboratory-scale stabilization tests (including TCLP testing of the stabilized material) to establish optimum conditions needed to pass the EPA leaching criteria for delisting of this waste.

The assessment team felt that a stabilization procedure should yield a nonhazardous residue that could be land disposed on available land at the plant site. Besides resulting in a considerable saving in disposal cost, this proposal would eliminate the need to use outside hazardous waste landfills if the stabilization method proved to yield a delistable waste. The nonhazardous material would be produced in an add-on chemical stabilization system located in the melt shop area, and the chemically stabilized material would be disposed of in an on-site dedicated landfill. A simplified schematic of a detoxification process for the K061 waste is shown in Figure 3.

In a recent (September 1988) update of the Armco K061 waste handling situation at the Butler plant, it was learned that Armco is having the AOD baghouse dust (about 10% of the total K061 waste) briquetted offsite and subsequently blended into the EAF feed with satisfactory operating results to date. Currently, the EAF steel product mix at the Butler plant includes a significant percentage of carbon steels, such that the venturi scrubber sludge has a high enough percentage of zinc to permit acceptance of the sludge by a zinc reclaimer. Armco is presently able to recycle all of the K061 waste generated at the plant.

TABLE 2. CAPITAL AND OPERATING COST ANALYSIS FOR PROPOSED K061 WASTE STABILIZATION SCHEME AT THE ARMCO INC., BUTLER, PA PLANT

Capital equipment and facilities required for waste stabilization

Item	Cost, $
—Site preparation	$10,000
—Concrete mixing pad 20 × 25 × 1 ft thick; reinforced 35,000 psi RediMix concrete; side walls 30" high; open ends	8,500
—Shelter bldg over pad area; 30 × 40 × 10 or 12 ft high; prefab steel corrugated roof and sides (could be reinforced fiberglass) Double doors both ends; unheated Complete, erected	25,000
—Electrical and water in shed	3,000
—Storage bin for lime dust (approx. 5 days supply); 12 × 12 × 25 Cone bottom; w/slide gate spout discharge and covered top with pneumatic fill attachment	18,000
—Bob-Cat front end loader; 3/4 CY bucket dedicated to K061 service; totally enclosed operators cab with fresh air intake particulate filter	60,000
—Front end Rototiller-type self-propelled mixer, 4 ft working width; enclosed operators cab with fresh air intake filter. Dedicated to K061 treatment	120,000
—1-6CY dump truck	45,000
—1-Bob-Cat front end loader for landfill operation	40,000
—1 Compacter, sheep-foot or equal	35,000
—1-Troxler Nuclear moisture gage, Model 3411	3,000
—2 Soil Test Penetrometers, Model CL-700 for compaction	100
Sub-total	367,600
20 percent contingency	73,500
Total capital	$441,100
Rounded	$442,000
Above estimates based on 1983–84 data; updated for 6 percent increase for labor, materials, and overhead, per annum	$526,000

Capital costs (on site stabilized waste disposal)

Landfill design based on EPA minimum technology guidance for single liner secure landfill (EPA/530-SW-85-013, May 24, 1985)

Item	Cost, $
Landfill installation cost, 11.25 acres × 100,000/acre[a]	1,125,000
Total capital costs (for stabilization facility and on-site secure landfill)	1,651,000
Cost of acquiring a RCRA Part B permit for an on-site TSDF[b]	100,000
Total capital cost	$1,751,000

Operating costs:

Item	Cost, $/Year
Lime kiln dust:[c] 11,000 TPY @ $10/ton delivered	110,000
Labor: $7.50/ton EAF waste[c]	83,000
Proprietary stabilizing materials (assumed)	10,000
Onsite disposal cost: 22,000 TPY @ $10/ton [3]:	220,000
Total operating cost	$423,000

Annual pre-tax operating savings of this option over present annual K061 disposal costs: $1,000,000-$423,000 = $577,000.

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[a] Based on actual costs obtained for new synthetic liner-equipped, leachate collection landfills; includes excavation, site preparation, membrane liner installation, and leachate collection and storage system.

[b] Armco estimate.

Feasibility Analysis Step

Based on the assessment team's evaluation of the available options, stabilization of K061 waste in an inpermeable matrix and disposal in an on site dedicated nonhazardous waste landfill, while not waste reduction, was believed to be the only technically viable option available to Armco. The assessment team proceeded to evaluate the economic viability of this option based on a study grade cost estimate. This economic evaluation follows.

The proposed alternative K061 waste treatment scheme involves treating a blend of 90% venturi scrubber sludge and 10% baghouse dust (approximately 11,000 TPY total, see Figure 2) with an equal weight of lime kiln dust and a small proportion of chemical additives (approximately 1% of the total mix) in an on-site blending operation. (Additives such as sodium silicate that would react with chromium to form an insoluble chromium silicate.) The EAF dust, sludge, and lime kiln dust are thoroughly mixed and then blended with additional water and appropriate special additives to approach within ±3% of the optimum water content (20–25%). This procedure was carried out to approach the desired physical and chemical properties in the final stabilized product.

The K061 waste stabilization scheme described has been subjected to a detailed capital and operating cost analysis. The information developed in this analysis is shown in Table 2.

Capital payback period available for this option (based on pre-tax annual savings) equals capital cost divided by net annual savings i.e., 1,751,000/1,000,000 = 3.0 years. Based on an economic life of 5 years (20% amortization per year), the internal rate of return is 20% [2]. The annual cost of stabilized waste preparation and disposal under this option is ($423,000 + 350,000)/22,000 or $35/ton, as compared to the current disposal cost of $100/ton.

A preliminary report presenting the K061 waste stabilization option described (together with the economic analysis) was given to Armco's Butler plant environmental engineering personnel for their comments. Armco agreed with Versar's findings that this option (chemical immobilization of EAF dust and sludge, with subsequent delisting of the treated waters and disposal in a dedicated on site nonhazardous landfill) was the only feasible option (from both a technical and economic standpoint) available to them (source reduction and recycle/reuse options being ruled out). Armco also noted that, based on their own limited laboratory studies on EAF sludge immobilization, it may not be possible to satisfactorily immobilize hexavalent chromium using this technique. More extensive laboratory studies will be necessary to answer this point. In addition, it is noted that chemical stabilization of RCRA F006 electroplating sludge containing comparable or higher levels of chromium together with organics and other extraneous materials has been successfully demonstrated to meet TCLP criteria for total chromium [*4*].

The Versar assessment team recommended that the Armco, Butler main plant seriously consider the possibility of implementing the waste detoxification option for melt shop K061 waste. Waste generated by the EAF/AOD operations in the melt shop was being disposed of at the rate of 11,000 TPY in offsite TSDFs at cost of $100 per ton. With source reduction and resource recovery options not available to reduce the quantity of this hazardous waste, the alternative proposed by the assessment team was to convert the material into a nonhazardous waste using a chemical stabilization technique, have the waste delisted by EPA, and dispose of this material in an on site dedicated landfill. A preliminary estimate of the cost of this option indicated a favorable payback period i.e., approximately 3 years with an internal rate of return of about 20%. Further, the disposal cost using this option was estimated as $35/ton of treated waste compared to $100/ton for the current cost of disposal of the raw waste. It was therefore recommended that this option be pursued further, with an initial bench-scale effort to establish the appropriate waste stabilization technique.

PLANT NO. 2 WASTE REDUCTION ASSESSMENT

Based on the information received by the assessment team, process and waste handling operations at Plant No. 2 were: the plant consists of a stainless steel strip annealing and pickling operation line for processing of series 300 and 400 stainless steels, and a waste acid neutralization plant. The facility anneals and pickles 300 and 400 series stainless steels. The plant pickling line pickles only Armco's stainless steel strip products and is composed of a Kolene treatment tank where the annealed steel sheet is treated with Kolene (a highly concentrated mixture of sodium hydroxide and potassium hydroxide) for descaling, a Kolene quench tank, two water rinse tanks in series, a nitric-hydrofluoric acid pickling tank, a final rinse tank, and a fume scrubber. A simplified schematic of the line is shown in Figure 4.

In the operation of the plant, stainless steel strip is received from the main plant located about 2 miles away. The stainless steel strip is first annealed and then descaled by the Kolene treatment, where oxide scale is removed by molten NaOH/KOH treatment at 800°F. The descaled strip is then rinsed to remove caustic materials and passed through a pickling operation where it is treated with a solution consisting of 2–4% hydrofluoric acid and 8–10% nitric acid. The pickled steel strip is then rinsed and coiled for shipment. The air emissions from the Kolene treatment and pickling acid tanks are all controlled by the use of wet scrubbers.

There were two corrosive waste streams (RCRA listed wastes K062) generated. The Kolene rinse water is highly alkaline and contains sodium and potassium hydroxides, sodium and potassium carbonates, and chromates resulting from some oxidation of the chromium on the steel surface during the Kolene descaling treatment. Chromate levels are below 200 ppm, and the spent rinse water has a pH of about 12. Spent pickle liquors and rinse waters from the pickling operations have a pH of about 2 and contain dissolved metals, nitrate, and fluoride. Approximately once per week, spent pickling acids (HF and HNO_3) are drained from the pickling tub, fresh acids are added, and a portion of the dumped spent acid is recycled. The spent pickle liquors contain 0–2% hydrofluoric acid and 0–8% nitric acid. They also contain dissolved nitrates and fluorides of cadmium, nickel, chromium, and iron. The excess spent pickle liquor is combined with the pickling line rinse water prior to being sent to the wastewater treatment facility. Average composition of the spent pickle liquor/rinse water stream over a one-week operation (which includes a once-per-week dump of the spent pickle liquor into the combined wastewater stream) is given as:

Parameter	Average Concentration, mg/l
Cr (trivalent)	164
Ni	47
Cd	<0.02
Fe	1,110
F	1,100
pH	~2.0

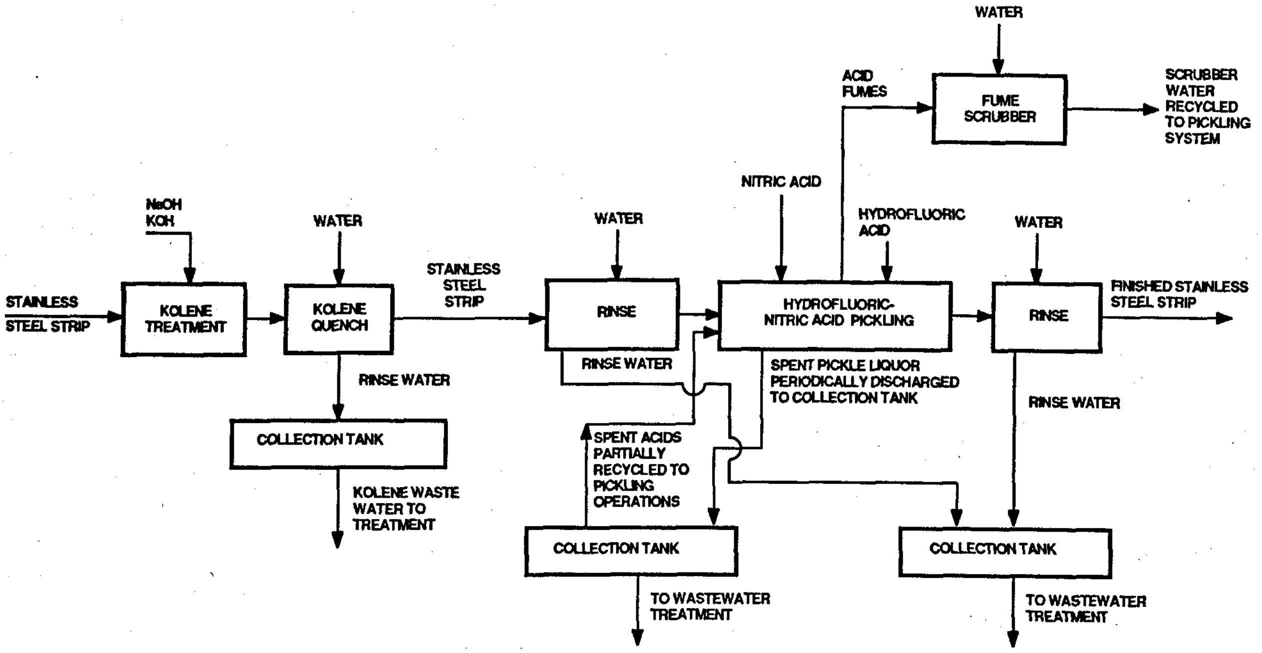

Figure 4. Simplified schematic of existing stainless steel surface treatment and pickling processes—Armco Plant No. 2, Butler, PA.

Volumes of wastes generated were about 5,000 gallons per week of the spent HF/HNO_3 pickle liquor are disposed of to the pickling line wastewater treatment system one batch basis. The combined wastewater stream from pickling operations including rinse waters and spent pickling acids, averages 150 gpm. Approximately 45 gpm of alkaline Kolene process rinse water was treated and disposed of.

Assessment Step

This phase of the waste reduction assessment began with a detailed inspection of the plant area by the Versar team. During this visit, the process flow was traced from the point of waste generation to the discharge of the treated K062 waste.

The hazardous waste management practice at Plant No. 2 involved pumping the combined spent acid and rinse water stream to the wastewater treatment plant where this stream is combined with treated Kolene waste and then neutralized. Raw Kolene rinse water is treated as follows: excess ferrous sulfate heptahydrate and sulfuric acid are added to the stream in a mix tank with about 80 minutes retention time. The ferrous ion reacts with chromate to reduce hexavalent chromium to trivalent chromium salts. The waste pH following treatment is approximately 4. The treatment of the combined waste stream was: the wastewater was pumped to a mix tank where slaked lime is added. The final pH after lime addition is about 8. The addition of lime causes the heavy metals present to precipitate as hydroxides and the fluoride to precipitate as calcium fluoride. The resulting mixture of treated wastewater and precipitated solids was treated in a second mix tank where coagulant is added and the stream is then fed to two 30-foot diameter clarifiers operated in parallel. The clear overflow from the clarifiers is discharged to the NPDES permit-controlled outfall (a local creek), and underflow is fed to two vacuum filters operated in parallel. Solids recovered from the filters (nonhazardous) were disposed of to an off site landfill and the filtrate was recycled to the treatment process.

The current treatment system yielded a treated wastewater containing about 21 ppm dissolved and suspended fluorides and negligible levels of heavy metals. The plant's present NPDES (Pennsylvania NPDES Permit #PA0006343) wastewater discharge permit requires that, effective at the end of 1988, the level of fluoride in the

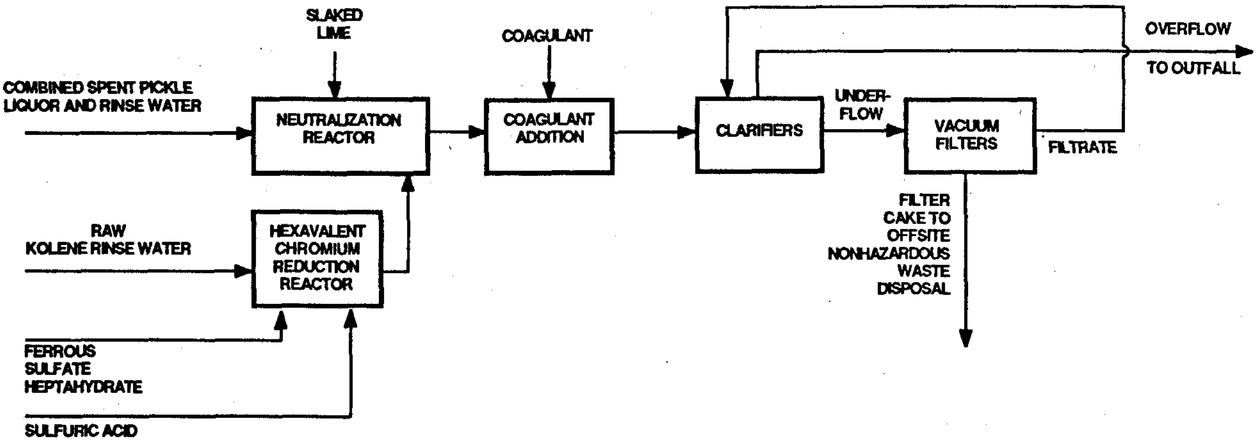

Figure 5. Simplified schematic of present wastewater treatment system, Armco Plant, Butler, PA.

final effluent (outfall 001) be reduced to 7 ppm. Figure 5 is a simplified schematic of the existing Plant No. 2 wastewater treatment system.

A review of possible waste reduction options at Plant No. 2 showed that Armco was already employing a source reduction technique by recycling a portion of the spent hydrofluoric acid/nitric acid pickling both to the pickling tank (see Figure 4). There did not appear to be any other major source reduction options available at the plant. In considering the possibility of recycle/reuse as a waste reduction option, the sludge resulting from treatment of the combined plant pickling line wastewater streams was studied. This sludge is a mixture of calcium sulfate, calcium fluoride, and small quantities of heavy metal hydroxides and there appeared to be no potential for reuse of this material. The raw waste, however, does contain a constituent that could be converted into a useful product—fluoride ion. Recovery of this ion as calcium fluoride (fluorspar) would require some modification of the existing treatment system.

The assessment team felt that an opportunity existed for recovering and utilizing calcium fluoride from the spent pickling acids and rinse water waste streams. The main plant melt shop presently purchases about 1,000 tons per year of fluorspar for use as a furnace flux material in the EAF steelmaking process with the current cost for this material being approximately $100 per ton at the plant. (Metallurgical grade material containing approximately 80% calcium fluoride is purchased in briquette form by Armco.) The assessment team proposed a waste reduction option for potential recovery of calcium fluoride wherein the combined plant wastewater stream at pH ~2 (excluding the treated Kolene waste) is treated with slaked lime at a controlled rate so that pH ~2.5 is not exceeded. Calcium fluoride would be selectively precipitated, and at this pH, fluoride solubility data in the literature indicate that a level of 65 ppm dissolved fluoride could be achieved. With about 1,100 ppm dissolved fluoride in the raw wastewater, approximately 95% of the fluoride is expected to precipitate. This is equivalent to about 1,300 tons per year of calcium fluoride potentially recoverable (based on 330 days per year operation), which more than equals the annual consumption of fluorspar flux in the EAF operation (930 TPY). Hydroxides of iron, nickel, and chromium are all highly soluble at pH values below 3.0 and thus would not co-precipitate with the calcium fluoride. Note that the recovered calcium fluoride was expected to assay better than 85% CaF_2, while the purchased metallurgical grade fluorspar averaged 77–80% CaF_2. This would actually enable the Melt Shop to reduce the amount of this flux added to each EAF heat by approximately 10%.

If the described option were to be put into operation by Armco, not only would the generation rate of sludge from K062 treatment be reduced (resulting in a saving in offsite sludge disposal costs), but a substantial potential savings in chemical purchases could be made. At the time of the assessment, Armco was disposing of approximately 4000 tons per year of nonhazardous sludge from Plant No. 2 wastewater treatment (in an offsite landfill) at a cost of $228,000 per year.

The necessary process modifications needed to recover solid calcium fluoride are shown in simplified schematic form in Figure 6 and consist of the combined A&P line #22 spent pickle liquor and rinse water discharge to be treated in the same waste acid neutralization system now used to generate the neutralized nonhazardous solids discharged off site and NPDES effluent to the outfall. However, the neutralization would be done in series in two stages, thereby effecting the recovery of a reasonably pure calcium fluoride in the first stage. After the first stage of neutralization, the presently treated Kolene waste would be combined with the partially neutralized waste pickle liquor/rinse water stream prior to final neutralization; the combined stream would then be neutralized and discharged to the outfall.

In the existing neutralization reactor (primary mix tank), slaked lime would be added to the combined pickle liquor/rinse water stream containing 1,100 ppm of fluoride, at a rate controlled to achieve a pH no higher than 2.5. At this pH, precipitation of fairly pure calcium fluoride would occur at the rate of 400 to 500 lb/hr. This slurry (with added coagulant) would then flow to one of the existing 30 foot diameter clarifiers where, after about

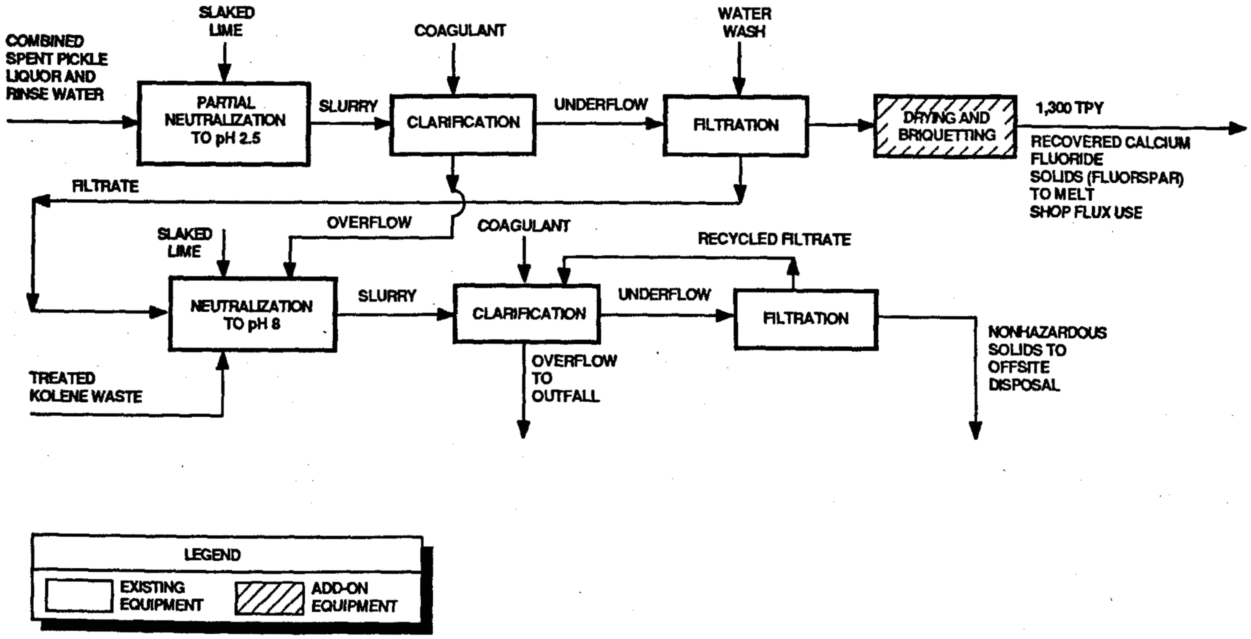

Figure 6. Proposed alternative treatment system for recovery of calcium fluoride from combined spent acid pickle liquor and rinse water at Armco Plant No. 2, Butler, PA.

one hour settling time, the underflow would flow to one of the two existing 6 ft × 6 ft vacuum belt filters. Following filtration, the filtered solids would be dried, briquetted and periodically transported to the melt shop area for use as flux in place of purchased fluorspar.

The combined clarifier overflow and filtrate from the vacuum belt filter and the separately treated Kolene waste would be pumped to the other existing 30 foot diameter clarifier where additional slaked lime and coagulant would be added to bring the final pH up to 8. At this pH, the residual fluoride and heavy metals would precipitate as calcium fluoride and hydroxides, respectively. It is expected that the achievable fluoride level would be near 7 ppm in the final effluent (the level required by December 31, 1988 by NPDES permit), because of the much lower amount of precipitated calcium fluoride available to be resolubilized in the second precipitation step. This would be an additional benefit achievable by this option. The settled slurry would then flow to the second existing 6 ft × 6 ft vacuum belt filter, where the solids are removed and discharged to a Vogel box. These solids would be nonhazardous and would be sent to off site disposal. The solids tonnage sent to offsite disposal would thus be reduced by approximately 30%, another economic benefit of this option. The clarifier overflow would be discharged to the local outfall.

It is believed that there is enough capacity available in the present clarifier/filter system in Plant No. 2 to allow the entire wastewater flow to proceed in series fashion through the two sets of clarifiers and filters. In the proposed first stage treatment step, calcium fluoride (with added coagulant) should settle much faster than the present calcium fluoride/metal hydroxide precipitate formed in the treatment plant. The latter material requires 8 to 10 hours residence time in the clarifier, while calcium fluoride (with added coagulant) should only need about one hour to adequately settle before the clarifier underflow is discharged to the vacuum belt filter.

Preliminary experimental verification and economic evaluation of this proposed calcium fluoride recovery option follow.

Feasibility Analysis Step

Versar performed bench-scale experiments to verify the technical feasibility of recovery of calcium fluoride from the spent pickling acid wastewater. A one-gallon sample

TABLE 3. CAPITAL AND OPERATING COST ANALYSIS FOR PROPOSED CALCIUM FLUORIDE RECOVERY SCHEME AT THE ARMCO INC., BUTLER, PA PLANT.

Capital costs	Installed Cost, $
Capital equipment requirements:	
• Drying (indirect gas-fired rotary dryer) and briquetting equipment to process 6.1 TPD of precipitated calcium fluoride (30% moisture) equivalent to 4.3 TPD of dry briquetted fluorspar equivalent.[a]	200,000
Existing equipment modifications:	
• Epoxy-coat one existing 30 ft diameter × 15 ft high carbon steel clarifier with 30 mil thickness of Bridgeport Chem. Corp. 6A70 (or equal) epoxy resin. Five-year warranty against liner failure Complete (labor and material)[b]	13,000
Epoxy-coat lime neutralization reactor tank[a]	2,000
• Rubber-line all exposed carbon steel parts of one existing 6 ft × 6 ft Ametek rotary vacuum filter (job done at vendor shop)[c]	50,000
• Rubber-line all piping and pumps exposed to pH 2.5 environment. Replace all valves and fittings with appropriate acid-resistant material[b]	30,000
Instrumentation changes required:	
• pH control on first neutralization stage required to be more sensitive and reliable than currently available at Plant No. 2 Estimate for pH equipment replacement[d]	5,000
TOTAL INVESTMENT COST	$300,000
Operating cost (330 days/year 8 hours/day for drying and briquetting operations)	Cost, $/yr
Precipitation/neutralization system: No significant increase in precipitation/neutralization system operating cost expected over present operating cost of wastewater neutralization system. Lime consumption should actually decrease because of closer pH control in neutralization operation	—
• Drying of 6.1 TPD precipitated calcium fluoride (dry 70% solids stream to <1% moisture in indirect gas heated rotary dryer using natural gas firing). With cost cost @ 4.00/MM BTU and energy utilization efficiency of 50%, drying cost is $2.40/1000 lb feed	1,000
• Briquetting of dried calcium fluoride @ $1.00/1000 lb feed to one-inch, roughly spherical briquettes (no binder required)	3,000
• Direct labor and supervision (0.6 persons @ $20/hr)	29,000
• Maintenance costs (labor and materials) for drying and briquetting equipment @ $0.50/1000 lb feed	4,000
TOTAL ANNUAL OPERATING COST	$46,000
Savings due to replacing purchased fluorspar, 1000 TPY @ $100/ton	$100,000
Savings due to lower cost of offsite landfill disposal ($228,000/yr × .30)	68,000
GROSS ANNUAL SAVINGS (Pretax)	$168,000/year
Net annual savings = $168,000-$46,000 = $122,000/year	
Payback period required: 300,000/$122,000	2.5 years

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[a] Vendor equipment estimates and assessment team installation cost estimates.
[b] Estimate provided by Tank Coatings, Inc., Pittsburgh, PA.
[c] Estimate by Rubber-Covered Products, Smithfield, RI.
[d] Assessment team estimate.

of spent hydrofluoric/nitric acid pickle liquor (not diluted with rinse water) was obtained from the Armco Plant No. 2 pickling line facility during the detailed plant inspection visit. An initial small-scale experiment was performed on this sample.

One 20 ml sample of the spent HF/NHO_3 pickle liquor was treated with 1.07 grams of anhydrous calcium chloride. The calcium chloride was dissolved by stirring into the pickle liquor. The pH of the resulting solution was then recorded as 1.67. The solution was then adjusted to pH 2.1 with saturated lime water. About 100 ml of lime water was added to raise the pH to the desired value. A *white precipitate (possessing a greenish tinge)* of calcium fluoride slowly formed and settled from the solution over about a one-hour period. The slow settling of the finely divided calcium fluoride indicates the need to add a coagulant (such as alum) in relatively small quantities, i.e., <100 ppm, to achieve rapid agglomeration and settling of the precipitated material. The solution was then filtered and samples of the filter cake and filtrate were forwarded for analysis. The filtrate was then treated with additional lime and lime water until pH 8 was reached. The solution was then again filtered, and samples of the filtrate and filter cake were forwarded for analysis.

Analyses for fluoride, nitrate iron, total chromium, hexavalent chromium, and nickel were then run on the two filter cake and two filtrate samples resulting from the above experiment. Results indicate that a relatively pure calcium fluoride material can be selectively precipitated at pH 2.5. Analysis of the material produced at this pH indicated about 80–85% calcium fluoride, approximately 13% iron fluoride, and about 1% chromium as chromium fluoride. This material should be directly usable as fluorspar flux (following drying and briquetting) in the EAFs at the melt shop and this recycle option appeared to be technically feasible.

In this recycle option, the assessment team proposed use of the existing lime neutralization reaction tanks, clarifiers, and filters available in the present wastewater treatment system. In order to handle the pH 2.5 wastewater, which is quite corrosive to carbon steel, it was proposed to epoxy-coat the existing lime mix tank, the clarifier, and to rubber-cover all exposed parts of one rotary vacuum filter, as well as all interrelated piping and pumps. All valves and fittings exposed to the pH 2.5 environment would be replaced with suitable acid-resistant materials. The other existing clarifier and rotary vacuum filter system exposed only to a pH 8 environment would continue to operate as carbon steel units. Since one clarifier/vacuum filter system can handle the present wastewater flow, if one of the other sets of these units were to go down for repairs, there would always be redundancy available in this system, i.e. the clarifier/filter system operating in the pH 2.5 mode could immediately switch to pH 8 operation (full neutralization without calcium fluoride recovery), in the event either of the other clarifier or filter units went down. As a further backup in the event of unavailability of this system for recovery of fluorspar, a suitable quantity of commercial fluorspar would always be kept on hand in the melt shop. It is envisioned that the revamp of the process units and related equipment would be accomplished during a plant turnaround, i.e., over a two-week period.

The calcium fluoride scheme described above has been subjected to a detailed capital and operating cost analysis. The information developed in this analysis is shown in Table 3. The payback period shown is shorter than is the usually acceptable yard stick for favorable investment payback (3 years). Based on an economic life of 5 years (20 percent amortization per year), the internal rate of return is approximately 28 percent [2].

A preliminary report presenting the fluorspar recovery option for Plant No. 2 HF/HNO_3 pickling waste were presented to Armco's Butler engineering personnel at a meeting on August 29, 1986. Armco expressed considerable interest in this proposed option: selective recovery of calcium fluoride at a controlled pH of 2.5 with subsequent use of this material (fluorspar) as a metallurgical flux in the main plant melt shop. The implementation of this option was to be seriously evaluated by Butler management.

SUMMARY

The Versar assessment team determined that Plant No. 2 generates a spent HF/HNO_3 pickling acid/rinse water waste stream (K062) that is currently neutralized with lime, the waste solids disposed of in an offsite nonhazardous waste landfill (approximately 4000 TPY) at an annual cost of $228,000, and the treated wastewater disposed of to a local stream under a NPDES permit. Following is a resource recovery option that was recommended for this waste.

Recovery of the bulk of the fluoride ion present in the raw HF/HNO_3 spent acid/rinse water waste stream as calcium fluoride by selective precipitation using lime and controlling pH so that the latter not exceed pH 2.5 (approximately 95 percent of the calcium fluoride can be recovered by this method). After clarification and filtration, the recovered calcium fluoride (approximately 1300 TPY valued at $130,000 based on Armco's present purchase price for this material) is dried, briquetted and used as metallurgical flux in the melt shop operation, replacing presently purchased material. Following calcium fluoride recovery, the partially neutralized spent acid/rinse water stream is fully neutralized as is done in the present waste water treatment operation at Plant No. 2. In addition to recovering a valuable product (fluorspar) for in-plant use, implementation of the option would reduce Armco's solid waste disposal cost at Plant No. 2 by approximately 30 percent. Versar also believes that an additional benefit would be the ability of the final neutralization step (following the selective fluoride precipitation step) to achieve the fluoride discharge level at the NPDES outfall i.e., 7 ppm fluoride, by 1988.

The team recommended that Armco give serious consideration to retrofitting one existing clarifier and one rotary vacuum filter to convert these units for corrosion resistant operation in order to operate in a pH 2.5 environment. These units would always be available to operate in the present pH 8 full neutralization mode if either the other clarifier or vacuum filter are disabled and down for repairs.

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