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Project Summary

Waste Minimization Audits at Generators of Corrosive and Heavy Metal Wastes

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The USEPA is encouraging hazardous waste generators to develop programs to reduce the generation of hazardous waste. To encourage such programs the Agency's Hazardous Waste Engineering Research Laboratory is supporting the development and evaluation of a model hazardous waste minimization audit procedure. The procedure was tested in several facilities in the summer of 1986.

Waste minimization audits (WMAs) have been carried out in an electric arc furnace (EAF) specialty steelmaking complex. These audits were intended to develop waste minimization options for two hazardous waste streams at this facility: corrosive waste and heavy metals waste. Waste minimization options considered were in one of three categories: source reduction, recycling or treatment (in the same order of preference).

Application of WMA methodology to a corrosive waste stream (KO62) generated at one plant in this complex, resulted in the development of a promising recycling option for the recovery of calcium fluoride (fluorspar) which is directly usable as a metallurgical flux (replacing presently purchased material) in the EAF steelmaking process at this facility. Savings obtained by using this option (including $68,000 savings from a thirty percent reduction in offsite nonhazardous waste disposal, and $100,000 savings in purchased chemical costs) were estimated at $168,000 annually, and the proposed process could largely use existing process equipment.

Application of the WMA methodology to a heavy metals-bearing waste (EAF dust-listed waste KO61) generated at another plant in the steelmaking complex did not result in any viable source reduction or recycling options for this waste. However, a detoxification treatment step proposed for this material is economically attractive based on preliminary estimates, and bench-scale development of this option appears warranted.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The U.S. Environmental Protection Agency (EPA) is expanding its efforts to promote waste minimization activity in the private sector by providing technical assistance to generators of hazardous waste. As part of this effort, the EPA Office of Research and Development/Hazardous Waste Environmental Research Laboratory (ORD/HWERL), Cincinnati, Ohio, is promoting the development of a generalized or model waste minimization audit (WMA) procuedure and testing this procedure in actual production facilities agreeing to cooperate with the audit teams selected for this task. Initially, the following four hazardous wastes were selected by EPA/ORD/HWERL to be studied in this effort: 1. Corrosives; 2. Heavy metals; 3. Waste solvents; and 4. Cyanides.

In the full report, results are presented of WMAs conducted at generators of corrosive and heavy metals wastes. A specialty steel manufacturing complex agreed to provide host facilities for the reported WMA effort. This complex includes the following plants, which were audited in the present effort:

- An annealing and pickling facility for finishing stainless strip only. This facility is designated as Plant No. 1.
- Cold rolling, annealing and pickling facilities for finishing both stainless and electrical steel product strip. These facilities are designated as Plant No. 2.
- The melt shop employing electric arc furnaces (EAFs) for the manufacture of stainless and electrical steels, as well as hot rolling furnaces for fabricating these steels into product strip, and EAF emission collection and cleanup equipment. This entire facility is designated as Plant No. 3.

Description of the WMA Protocol

The function of the protocol is to force the use of a step-by-step procedure for conducting a WMA at a host site. The initial WMA protocol was developed in earlier work and was further refined during the present effort. The protocol is applicable to all three categories of waste minimization (source reduction, recycling, and treatment).

The teams employed in carrying out the audits were composed entirely of employees of outside consulting/engineering firms. After selection of the host facility, the following sequential steps were executed by the audit team:

1. Preparation for the audit
2. Host site pre-audit visit
3. Waste stream selection
4. Host site waste minimization audit visit
5. Generation of waste minimization options
6. Preliminary evaluation (including preparation of preliminary cost estimates) and ranking of options in three categories (effectiveness, extent of current use, application potential)
7. Presentation, discussion and joint review of options with plant personnel
8. Final report preparation and presentation to host site management

This protocol was used to conduct the WMAs, as summarized below.

Results of the WMA Conducted at a Generator of Corrosive Waste Audit at Plant No. 1

Following the selection of Plant No. 1 as a host site for a WMA for corrosive waste (listed waste K062), a pre-audit visit was made and process and waste treatment operations were directly observed. The Plant No. 1 facility consists of a stainless steel strip annealing and pickling line for processing 300 and 400 series stainless steels and a pickling waste water neutralization plant.

Following annealing of the stainless steel strip, this material is fed through the continuous pickling process. The strip is first treated in a Kolene bath (the latter a mixture of molten sodium and potassium hydroxides) at 800°F for initial dissolution of surface scale on the strip, followed by water quench and rinse tanks to cool and flush the treated strip, and then a nitric-hydrofluoric acid pickle using a mixture of 8-10 percent nitric acid and 2-4 percent hydrofluoric acid. Following a water rinse, the stainless steel strip is coiled and shipped. Air emissions from the Kolene treatment and acid pickling tanks are controlled through the use of fume scrubbers. The following waste waters are generated in the pickling process:

- A Kolene rinse water which 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. Approximately 45 gallons per minute (gpm) of Kolene rinse water is discharged from the process.
- Spent HF/HNO_3 pickle liquor waste. This stream is periodically dumped and replaced with a mixture of fresh HF/HNO_3 and recycled spent pickle liquor.
- Rinsewater from the HF/HNO_3 pickling operation. This stream is generated continuously from the rinsing operation.
- The combined spent pickle liquor and rinse water waste stream from the HF/HNO_3 pickling operations has a pH of about 2 and contains dissolved metals, nitrate and fluoride. The combined wastewater stream flow from the pickling and rinse tanks averages 150 gpm. Average composition of the spent pickle liquor/rinse water stream over a one-week operation (which includes a once-per-week dump of 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*

The Kolene waste rinse water and the combined spent acid/rinse water waste stream are treated as follows:

- Raw Kolene rinse water is treated in a mix tank with excess ferrous sulfate heptahydrate and sulfuric acid with about 80 minutes retention time. The ferrous ion reacts with chromate to reduce hexavalent chromium to trivalent chromium. The pH of the treated waste is approximately 4.
- The combined spent acid/rinse water waste and the treated Kolene rinse water are 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 is 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 outfall (a local creek) meeting the conditions of an NPDES permit and the underflow is fed to two vacuum filters operated in parallel. Non-hazardous solids recovered from the filters are disposed of offsite and the filtrate is recycled to the treatment process.

During the formal audit phase of this study at the Plant No. 1 acid pickling facility, process and waste treatment operations were intensively studied by the audit team. The use of various potential source reduction and recycling options was reviewed with plant personnel. Plant No. 1 already recycles part of the spent acid mixture to the pickling line, thus reducing fresh acid use. Based on the audit team's evaluation and discussions with plant personnel, there did not appear to be any other significant source reduction options available.

With respect to recycling, the present neutralization treatment of the combined

Plant No. 1 pickling line wastewater stream (KO62) generates a mixed sludge for which there is essentially no potential for reuse. The audit team determined, however, that the raw waste (the spent HF/HNO_3 pickle liquor/rinsewater discharged from the pickling operation) does contain a constituent (fluoride ion) that could be converted into a useful product-calcium fluoride (fluorspar). The electric arc furnace (EAF) facility at this steelmaking complex (designated as Plant No. 3) presently purchases about 1,000 tons per year of fluorspar for use as a furnace flux material in the steelmaking process. Current cost for metallurgical grade fluorspar (approximately 75-80 percent calcium fluoride) for flux use is $100 per ton at the plant. The audit team proposed a waste minimization option for recovery of calcium fluoride wherein the combined Plant No. 1 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 will precipitate selectively, and at this pH, fluoride solubility data indicate that a level of 65 ppm dissolved fluoride will be achieved. With about 1,100 ppm dissolved fluoride in the raw wastewater, approximately 95 percent of the fluoride will 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 calcium fluoride (fluorspar flux) in the EAF operation and Plant No. 3. Hydroxides of iron, nickel, and chromium are all highly soluble at pH values below 3.0 and thus would not be expected to co-precipitate with the calcium fluoride.

The combined spent HF/HNO_3 pickle liquor and rinse water discharge would be treated in the same waste acid neutralization system now used to generate the neutralized nonhazardous solids discharged offsite and NPDES effluent to the outfall. However, the neutralization would be done 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. The combined stream would then be neutralized and discharged to the outfall.

If the above described option were to be put into operation at Plant No. 1, not only would the generation rate of sludge from KO62 treatment be reduced (resulting in a saving in offsite sludge disposal costs), but a substantial potential savings in chemical purchases could be made. Plant personnel agreed with the audit team that this was a worthwhile option.

After a recycling option established for the Plant No. 1 corrosive waste, the preliminary engineering design and cost estimate for this option was developed. A preliminary estimate (using 1986 capital and operating cost data) of the economics of this recycling option indicates the following:

- Total capital cost (including new drying and briquetting equipment and retrofitting of one existing clarifier vacuum filter system to make it corrosion-resistant at pH 2.5) $300,000
- Annual operating cost $ 46,000/yr
- Savings due to replacement of purchased fluorspar $100,000/yr
- Savings due to lower cost of offsite waste disposal $ 68,000/yr
- Total potential savings $168,000/yr
- Estimated payback period 2.5 years
- Estimated internal rate of return (based on an economic life of 5 years) 28 percent

Audit at Plant No. 2

Plant No. 2 consists of cold-rolling equipment to convert raw stainless steel and electrical steel slabs into strip, annealing ovens, and a series of six countercurrent flow pickling lines which acid pickle stainless and electrical steel strip produced in the cold-rolling equipment as well as stainless and electrical hot-rolled steel strip produced in the EAF raw steel manufacturing facility. Its six pickling lines use HF, HNO_3, H_2SO_4, and mixtures thereof and have a total nameplate capacity of 1,833 tons per day of processed steel strip.

Emissions from all of the pickle lines are controlled by use of fume scrubbers. Following pickling, the treated strip is wound into coils and shipped.

The six pickle lines generate the following spent pickling acids: dilute spent sulfuric acid, dilute spent mixed sulfuric-hydrofluoric acid mixtures and dilute spent mixed nitric-hydrofluoric acid mixtures (also containing dissolved iron salts and traces of dissolved chromium, cadmium, and nickel), as well as rinse waters containing lower concentrations of these components. About 313,000 gallons of spent sulfuric acid, 144,000 gallons of spent sulfuric/hydrofluoric acid, 12,000 gallons of spent hydrofluoric/nitric acid pickle liquors and 9.7 million gallons of rinse water are generated in this facility per week. The average composition of the combined waste stream (in terms of critical metal and non-metal parameters) is as follows:

Parameter	*Average Concentration, mg/l*
Cr	*49*
Ni	*28.5*
Cd	*<0.02*
Fe	*500*
Fluoride	*39*
pH	*~2*

This stream also contains emulsified and free fatty oil and grease from the cold rolling operations at this facility. The combined wastewater discharge from Plant No. 2 is sent to a central treatment facility onsite where it is treated with lime to effect precipitation of metals as the corresponding hydroxides and removal of fluoride as calcium fluoride. The treated wastewater slurry is then pumped to a series of onsite large lagoons where the suspended solids are removed by sedimentation and the treated wastewater is then discharged to the outfall. The precipitated solids meet EP-toxicity test levels for hazardous metals and the treated wastewater is discharged to a local creek under an NPDES permit.

During the formal audit phase of this study at the Plant No. 2 acid pickling facility, the use of source reduction and/or resource recovery options was studied by the audit team. No source reduction options were identified by the audit team. Furthermore, the current neutralization treatment of the combined pickling and cold-rolling aqueous waste stream (listed waste KO62) generates a mixed metal hydroxide-gypsum-calcium fluoride sludge for which there is no reuse potential. The key to waste minimization at this plant is suitable segregation of selected spent acid wastes before these wastes are combined at the process building outlet flume (the latter discharging to a centralized wastewater neutralization process) — an option that plant personnel indicated would be highly disruptive to plant operations and costly as well. However, assuming that pickling waste stream segregation is feasible, the following waste minimization option is proposed by the audit team:

- As a recycling option segregate an appropriate amount of waste sulfuric acid pickle liquor (13.5 million gallons per year are potentially available from three pickling lines).* Two uses for this material were identified by the audit team:

— Reduction of hexavalent chromium in a bleed stream of venturi scrubber waste resulting from scrubbing of EAF dust in Plant No. 3.
— Reduction of hexavalent chromium in the Kolene waste in Plant No. 1.

Both of these uses presently employ purchased solid ferrous sulfate heptahydrate. Recycled sulfuric acid pickle liquor (containing 5 to 10 percent dissolved ferrous sulfate) is usable for this purpose.

The technical and economic feasibility of this recycling option was evaluated by the audit team. A preliminary estimate of the economics of this recycling option indicates the following:

● Total capital cost (including new tankage, piping, and pumps, a tank truck to haul the spent acid between the various facilities and suitable permitting)	$255,000
● Annual operating cost	$ 20,000/yr
● Savings due to replacing purchased ferrous sulfate heptahydrate with waste ferrous sulfate/sulfuric acid pickle liquor	$ 44,000/yr
● Savings due to lower lime usage for neutralization at Plant No. 2	$ 8,000/yr
● Total potential savings	$ 52,000/yr
● Estimated payback period	8.0 years

The payback period of eight years is almost three times the usually acceptable period of three years, making the proposed project distinctly unattractive from an economic standpoint. In addition to the obvious economic disadvantage of this option, plant personnel are concerned with the cost and disruption of decoupling the internal discharge points of this waste (in the pickling process building) needed to segregate the appropriate amount of this waste for recycle. No information was available from the plant to permit estimation of the cost of decoupling this waste quantity from the remaining waste streams discharged from the facility. However, since the use of this option does result in some waste minimization as well as a small but measurable extension in the life of the present waste lagoon disposal system (approximately 10 percent less calcium sulfate and metals-containing solids would be deposited in the lagoons), the audit team believes that the option should continue to be reviewed at Plant No. 2.

* Based on 300 days per year (43 weeks/yr) operation of the Plant No. 2 acid pickling lines.

Results of the WMA Conducted at a Generator of Heavy Metals Waste

During the pre-audit visit to this facility (designated as Plant No. 3) the audit team became acquainted with process operations at the EAF melt shop and the wastes generated from these operations. The melt shop contains three 165 ton capacity EAFs used to manufacture 300 and 400 series stainless steels and silicon steels, as well as one 175 ton argon-oxygen decarburizer (AOD) used to further refine the raw stainless steels. Steels leaving the furnaces are processed through continuous casting and hot-rolling operations to produce coils of strip which are sent to the acid pickling facility (Plant No. 2) for final processing. Production of stainless and electrical steels is approximately 270,000 tons per year.

The pre-audit visit yielded the following waste stream characterization and treatment information at:

- The three EAFs and the AOD at the melt shop generate about 8,000 tons per year (TPY) of particulate emissions (listed waste KO61).
- Of these emissions, approximately 7,000 TPY are removed from the EAF vent gases using venturi scrubbing; the remaining 1,000 TPY include EAF fugitive emissions as well as emissions removed from AOD vent gas, and are recovered in a baghouse.
- The venturi scrubber slurry is clarified and filtered with the filter cake, containing about 30 percent water, discharged at the rate of 10,000 TPY.
- The combined EAF dust and sludge (listed waste KO61) leaving the plant totals about 11,000 TPY and is sent to offsite hazardous waste landfills at an annual cost of approximately $1.0 million.

During the detailed audit phase of this study at Plant No. 3, the use of source reduction and/or recycling options for EAF dust emissions was reviewed with plant personnel. The following information was developed which discouraged further exploration of these waste minimization options for the KO61 waste generated at the plant:

- With the primary steel products of this facility being 300 and 400 stainless grades, there will always be significant levels of the following hazardous metals in the EAF dust: chromium and nickel (because of the alloying requirements of stainless steels), cadmium and lead. Contributions to these metals in the EAF dust come from the scrap feed as well as from the alloying additives. These EAF dust constituents are expected to always generate levels of one or more of these hazardous metals in excess of the presently allowable RCRA levels in leachate from the TCLP procedure (using acetate buffer). Source reduction is therefore not an available option to the plant.
- Plant No. 3 has made a number of attempts (without success) to recycle EAF dust to the steelmaking furnaces. Plant personnel also indicated that because of the volume of dust generated and the sensitivity of the steel product quality to tramp elements in the recycled dust, it is unlikely that a large percentage of this waste could ever be recycled to the process.
- With respect to use of the KO61 waste by a metals reclaimer, the principal ingredient of value (zinc) is only present to the extent of 8 to 10 percent in the Plant No. 3 EAF dust. In order for EAF dust to be economically attractive to reclaimers, it should have at least 20 percent zinc and preferably nearer 50 percent. Additionally, internal recycling of the EAF dust, which would tend to enrich the zinc content of the residual material, is presently not available to Plant No. 3 due to factors discussed above.

No source reduction and/or recycling options appear to be available to reduce the quantity of KO61 waste generated by this plant. The last resort is an alternative treatment step proposed by the audit team which appears to be the only option available for this waste stream and is summarized as follows:

Plant No. 3 would (1) convert the material into a nonhazardous waste using a chemical stabilization technique (using lime kiln or cement kiln dust and water blended with the EAF dust to generate solidification reactions and create an essentially insoluble matrix), (2) apply to have the waste delisted by EPA, and (3) dispose of the delisted material in an onsite dedicated landfill.

A preliminary estimate (using 1986 capital and operating cost data) of the economics of this option (for 10-year onsite disposal) results in the following:

- Total capital cost — $1.75 million
- Annual operating cost — $0.42 million/yr
- Estimated payback period — 3 years
- Estimated internal rate of return (based on an economic life of 5 years) — 20 percent
- Present annual KO61 waste generation rate — 11,000 TPY
- Proposed annual treated KO61 waste generation rate — 22,000 TPY
- Cost of treatment and disposal of waste — $35/ton
- Annual savings (over amortized life of treatment plant and onsite landfill), if this option was implemented — $227,000/yr

The disposal cost of KO61 waste using this treatment option is estimated at $35/ton of treated waste compared to $100/ton for the current cost of disposal of the raw waste even though the treated waste generation rate has doubled. It is therefore recommended that this treatment option be pursued further with an initial bench-scale effort to establish the appropriate waste stabilization technique.

It should be noted that plant personnel are in agreement with this assessment of available waste minimization options.

Conclusions

The following conclusions can be drawn based on the study summarized herein:

- The WMA methodology can be successfully applied to the minimization of hazardous waste, in this case corrosive waste (KO62), in at least one industry — the specialty steels segment of the EAF steelmaking industry. Application of the WMA protocol to a plant in this industry (a stainless steel pickling facility in an EAF steelmaking complex), resulted in the identification of a technically and economically feasible recycling option for the recovery of fluorspar (calcium fluoride) from a corrosive waste stream. The fluorspar would be used internally in place of purchased material. Use of this waste minimization option results in savings of $168,000 annually and a 30 percent reduction in final waste disposal volume.
- Application of the WMA methodology to another corrosive waste generated at another steel pickling facility in the same steelmaking complex, resulted in the development of a recycling option requiring segregation of a portion of this waste (waste ferrous sulfate/sulfuric acid pickle liquor) for internal recycle replacing purchased ferrous sulfate heptahydrate. However, this option is not economically feasible and this disadvantage outweights the principal advantage of a small prolongation of the life of the onsite facility for disposal of neutralization sludge from present waste treatment.
- An attempt to apply the WMA methodology to another hazardous waste stream: heavy metals — containing EAF dust (KO61) generated in the EAF steel plant at the same steelmaking complex, could not be considered as successful inasmuch as both of the more preferred waste minimization approaches (source reduction and recycling), were not technically feasible in this case. However, the identified treatment approach: detoxification of the waste by onsite chemical stabilization/solidification treatment, followed by onsite disposal in a dedicated landfill, appears to be worth investigating further based on the results of a preliminary technical and economic evaluation of this option.
- It is believed that the on-site audit (employing the WMA methodology developed in this study) is a distinctly useful tool for waste minimization due to the one-to-one contact with the industrial waste generators by qualified engineering professionals on the audit team.

This Project Summary was prepared by staff of Versar, Inc., Springfield, VA.
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The complete report, entitled "Waste Minimization Audit Report: Case Studies of Corrosive and Heavy Metal Waste Minimization at a Specialty Steel Manufacturing Complex," (Order No. PB 88-107 180/AS; Cost: $13.95, subject to change) will be available only from:
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