HAZARDOUS METAL WASTES: LANDFILL ALTERNATIVES

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by
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ABSTRACT

This study was proposed to find technologically available processes which could be used as economically feasible alternatives to land disposal of hazardous wastes. The scope of the study was limited to heavy metal contaminated hazardous wastes generated in Missouri. Data on 95 such waste streams were taken from the Missouri Department of Natural Resources' Hazardous Waste Generator Registration Files. Economic criteria reduced the number of streams under consideration to twelve. Two streams, an electric arc furnace flue dust and an electroplating wastewater treatment sludge, were chosen for detailed study.

An electrothermic reduction roast process called the Plasmazinc process was proposed to recover iron, lead and zinc from the electric arc furnace flue dust. In this process, an electrically generated plasma is used to supply heat to a low shaft furnace which contains the dust and an excess of coke. A reducing atmosphere of carbon monoxide and hydrogen is maintained throughout the process so that lead and zinc can be collected as metals in a splash condenser. Iron is tapped from the bottom of the furnace. This process was developed by SKF Steel of Sweden. A profitability analysis for a Plasmazinc plant capable of processing 91,000 kkg of dust annually suggested that the dust would have to be delivered to the plant free of charge for it to be feasible. The discounted cash flow rate of return for this case was found to be 15.1%.

A reverse osmosis unit integrated into the rinsing system was proposed to recycle nickel plating salts currently contaminating the electroplating wastewater sludge. As suggested by the generator, the 99.9% reduction of nickel in the sludge which would result could be sufficient to induce the EPA to grant a regulatory exclusion for the waste. The estimated savings in disposal and plating chemicals' costs would effect a projected discounted cash flow rate of return of 15.8%.

Elimination of these two streams would reduce the amount of hazardous waste generated in Missouri and disposed of on or in the land by 10%.

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I. INTRODUCTION

Industry in the United States today produces a vast array of goods and services, all of which have been deemed, through economic considerations, necessary and desirable by the general public. The production of these goods and services has allowed the United States to build an economy which affords a standard of living to its consumers that is second to none. Unfortunately, wastes from the production and use of many of these goods and services are toxic, corrosive, flammable or otherwise hazardous to manmade and natural environments.

In recognition of and response to the environmental threats posed by these wastes the federal government passed the Resource Conservation and Recovery Act (RCRA) in 1976. This legislation provided for the definition and regulation of hazardous wastes on the federal level and was implemented through the Environmental Protection Agency. Further, the RCRA urged the states to enact their own programs for the management of hazardous wastes. Thus, in 1977, the Missouri General Assembly passed the Missouri Hazardous Waste Management Act which became effective in July, 1980.

Prior to the passage of the RCRA, Hazardous wastes were generally disposed of in the least expensive manner that the generator felt conscionable. These disposal practices included open dumping on land and into waterways, attempts to securely landfill, and thermal destruction. The first of these was obviously unsatisfactory and almost always disastrous. The current problems resulting from spreading dioxin contaminated oils on land throughout Missouri is adequate testimony. Attempts prior to RCRA to securely landfill hazardous wastes were also unsatisfactory most of the time, though not always due to poor landfill design. The problems associated with the Love Canal landfill were primarily the result of the disturbance of the landfill's clay cap and liner during construction projects undertaken by the City of Niagara Falls, New York. Had regulations been in effect which prohibited such uses of closed hazardous waste landfills these problems might have been avoided.

The two incidents mentioned above have been major contributors to the development of public opinion against the disposal of hazardous wastes on or in the land. The general public considers hazardous waste landfills as great risks to the environment, especially to groundwater and property values. People believe the potential losses outweigh the economic advantages made available by this relatively inexpensive method of disposal. Many people in Missouri and the U.S.A. feel that all landfilling of hazardous wastes should be stopped immediately. Most people believe that many of the hazardous wastes being buried today could be reclaimed or recycled, thus conserving natural resources and reducing the risk to the environment. Once these materials are buried it is intended that they stay buried. They are therefore lost from a recycling standpoint but continue to pose an indeterminate liability problem.

When the Missouri Hazardous Waste Management Act went into effect in July of 1980, the Missouri Department of Natural Resources received several applications to develop hazardous waste landfills in Missouri. Due to public apprehension about these potential landfills, a special legislative session of the Missouri General Assembly was called in the fall of 1980 to revise the Missouri Hazardous Waste Management Act. One of the outcomes of this session was the establishment of the Hazardous Waste Management Task Force. The purpose of this task force was to recommend a comprehensive waste management program which would "minimize the need for such disposal in the land of the state." The task force, in conjunction with private citizens and government officials, surveyed industry and held a public hearing in an effort to implement the views of all sectors into its recommendations. Those recommendations were submitted to the Missouri General Assembly in September of 1981.[1] The need to minimize landfilling of hazardous wastes is stated throughout the report. Also recognized in the report is the fact that the Missouri Department of Natural Resources does not have adequate resources to actively undertake development of alternatives to hazardous waste landfilling. Thus, recommendation #3 states:

> "The Department of Natural Resources should initiate a waste management research program and a technical assistance program in cooperation with the University of Missouri. This program should be

> designed to stimulate treatment and resource recovery while minimizing land disposal of hazardous wastes."

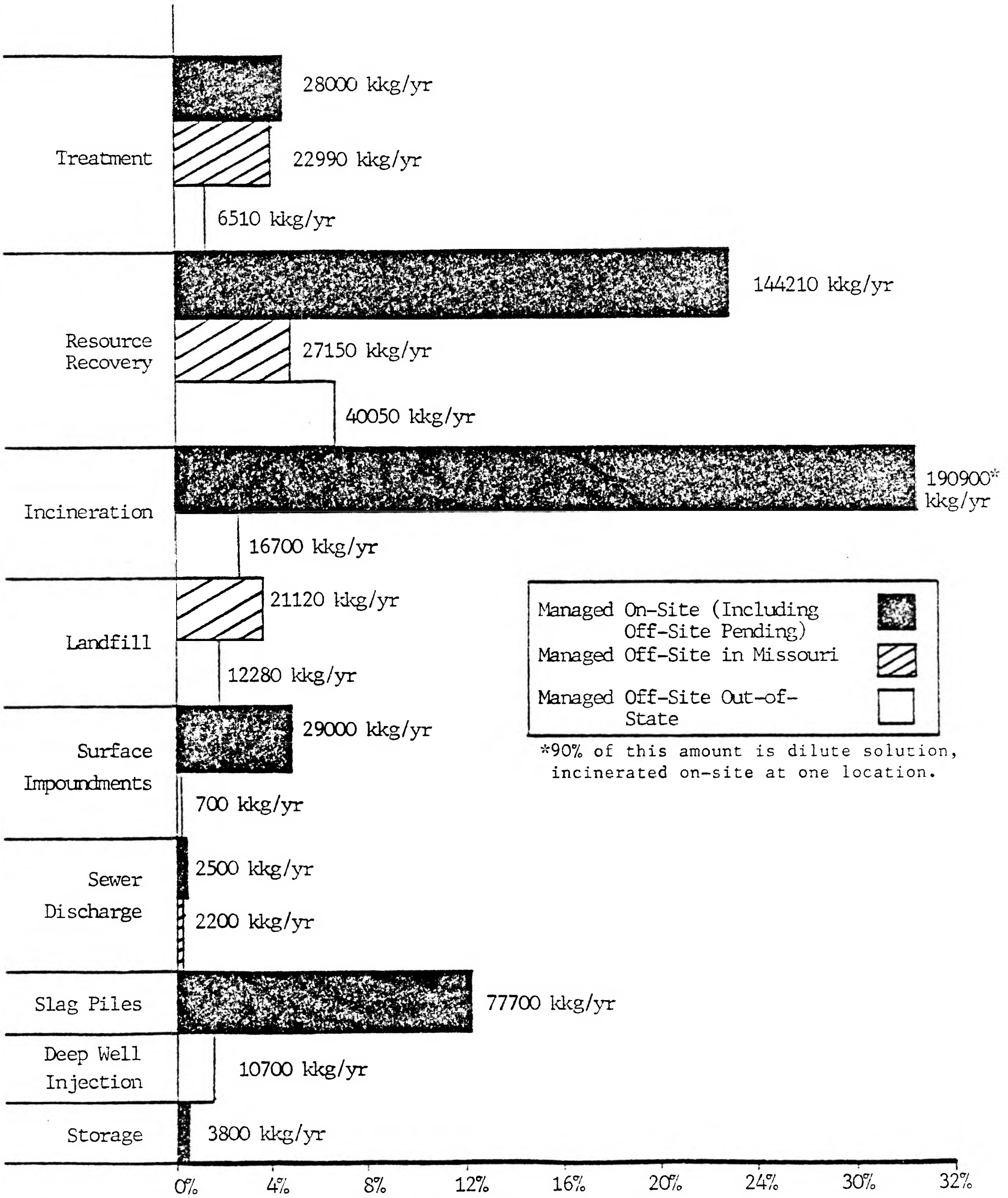
This study is a result of the recommendation.

Approximately 700,000 metric tons of hazardous wastes are generated annually in Missouri. This includes about 45,000 metric tons of waste oil. Disregarding the waste oil, Figure 1 shows that about 24% of the hazardous waste generated in Missouri is disposed of on or in the land (20% in state, 4% out-of-state).[1] This includes landfills, surface impoundments, slag piles, and deep well injection. These are the disposal methods that pose the greatest risk of allowing hazardous contaminants to migrate away from the disposal site through the groundwater.

The 76% of the waste that is disposed of by alternate methods is indicative of industry's considerable efforts to minimize land disposal. Each of these alternate methods achieve at least one of the following goals:

(1) recovery of valuable materials;
(2) recovery of energy;
(3) reduction of hazard;
(4) reduction of volume.

The first two goals obviously provide the potential for economic gain. The third and fourth also provide this potential through possible reductions in disposal costs. Any of these are goals that an alternative disposal method must be designed to achieve if it is to be attractive to



*90% of this amount is dilute solution, incinerated on-site at one location.

Figure 1. Amount of Missouri's Largest Generators' Hazardous Waste by Disposal Method as Percentage of Total Hazardous Waste Generated in Missouri.

industry. Of long term benefit, the use of these alternate methods of disposal stands to reduce the liability of the generator by reducing the risks to the environment.

The purpose of this study is to ascertain what technologically available processes could be economically used as alternate disposal methods for a few of the hazardous waste streams that are currently being disposed of in or on the land. In this study only streams that are contaminated with heavy metals are addressed due to the fact that they comprise the bulk of the hazardous waste generated in Missouri that is landfilled. Two streams, an electric arc furnace baghouse dust and a electroplating wastewater treatment sludge, have been chosen for detailed study. The results suggest that these streams could be economically disposed of by alternate methods. Suggestions for some of the other streams are included.

II. COLLECTION AND REDUCTION OF DATA

Data files kept by the Missouri Department of Natural Resources Waste Management Program contain the most comprehensive collection of information concerning hazardous wastes generated in Missouri. This information was made available for this study as a result of a cooperative agreement between the Waste Management Program and the researcher and his advisor. It has been requested by the hazardous waste generators that some of this information be kept confidential by the Department of Natural Resources so as to protect proprietary process information. Thus a major stipulation of the cooperative agreement is that no confidential information be presented that would connect a given generator with a given waste stream. The use of hazardous waste generator names and detailed waste stream composition data will be kept to a minimum. For the most part an arbitrary numbering system will be used to identify individual streams.

Information potentially of value to this study is contained in three separate sets of files. These are:

(1) The Hazardous Waste Generator Registration Files;

(2) The Hazardous Waste Manifest Files;

(3) The Hazardous Waste Disposal Facility Logs.

The Hazardous Waste Generator Registration Files contain registration forms that were required after July 1, 1980 from all hazardous waste generators. These forms were used to estimate what and how much wastes were generated and how they would be managed. It was assumed that reported compositions and amounts were estimated averages.

The Hazardous Waste Manifest Files and Disposal Facility Logs primarily contain information that applies to each individual shipment of hazardous waste. The manifest allows tracing of the shipment from the generator through the transporter to the disposal facility. The Disposal Facility Logs acknowledge the receipt of the shipment and the method of disposal. Any data specific to these files concerning amount or composition does not necessarily reflect average or long term conditions.

If the alternate disposal methods sought in this study are to be proposed as long term solutions to the problems of land disposal, the basis for their design must be over the long term. It is assumed that shipment to shipment or season to season fluctuations need not be considered unless there is reason for special concern. Thus the decision was made to use the average data from the Hazardous Waste Generator Registration Files.

As expected, the data in the Generator Registration Files indicate that the majority of the hazardous wastes generated in Missouri are not landfilled. It would be desirable not to have to inspect every Generator Registration Form to find if that waste is landfilled. Further, it would be too time consuming to assess the recovery potential of every land-disposed hazardous waste stream. Some criteria for limiting the extent of this study was necessary.

The first step was to separate the land-disposed streams from the rest of the hazardous waste streams. The M.D.N.R. had divided all registered hazardous waste streams into 26 categories. Table 1 lists each of these categories along with the corresponding percentage of the total hazardous waste landfilled in Missouri that is landfilled from each category. A computer printout was developed which started with the acid streams, in order from largest stream to smallest stream, and printed out the generator I.D. number, the generator name, and the individual stream number. Then under the headings of landfill, resource recovery, treatment, incineration, or other, the quantity of each stream in kkg/yr was printed in the appropriate column corresponding to the reported methods of disposal. When all the acid streams had been tabulated, the computer repeated the above for the alkali streams and so on. This provided a convenient means of separating the pertinent generators, who disposed of their waste in landfills, from the other generators, who use alternate methods of disposal.

The computer results also provided the basis for limiting the scope of the study. Table 1 was developed from the printout. As can be seen from Table 1, the vast majority of M.D.N.R's categories account for less than four percent of the total hazardous waste landfilled in Missouri. All except one of the categories account for less than ten percent. The M.D.N.R. category of toxic metals from sources other than plating accounts for more than half of the total

TABLE 1

Percent of Total Waste Landfilled, by M.D.N.R. Category

Category	Percent
1) Acids	1.23
2) Alkalis	1.68
3) Asbestos	.21
4) Containers	1.40
5) Controlled substances	< .01
6) Cyanides	.05
7) Explosives	0.00
8) Organic halides	5.55
9) Organo-metallics	< .01
10) Industrial oils	7.60
11) Lubricating oils	.03
12) Transformer oils (PCB's)	1.61
13) Paint sludges	3.55
14) Pesticides (cancelled)	.15
15) Pesticides (RPAR)	2.24
16) Poisons (DOT)	3.83
17) Priority pollutants	.26
18) Halogenated solvents	.74
19) Non-halogenated solvents	1.48
20) Toxic metals (plating)	.70
21) Toxic metals (other)	54.18
22) Miscellaneous	1.76
23) Filter aids	1.26
24) Contaminated debris	1.84
25) Other organics	.31
26) Declared hazardous	8.33

hazardous waste landfilled in Missouri. It was judged that the category which contributed the most hazardous wastes to landfills would have the greatest probability of including major streams that could be disposed of by other methods. A major stream is an individual stream that contributes significantly to the total amount landfilled. Thus in a better than arbitrary fashion, it was decided to limit the scope of the study to the toxic metal streams. Toxic metal streams from the plating industry were included because of presumed similarities to some of the toxic metal streams from sources other than plating. Since many pigments have a high heavy metal content, paint sludges were also considered. These streams were disregarded, however, due to the nonspecific way in which most of their compositions were reported. Most of the composition data from hazardous paint sludge generators merely stated percent pigment, percent resin, percent solvent, etc..

In the fall of 1981, all the Hazardous Waste Generator Registration Files listing streams that were tabulated in either of the toxic metal categories under the disposal heading of landfill were investigated. Streams generated at rates less than 0.1 kkg/yr were disregarded. This resulted in a data base from 95 streams. The following information was recorded from the Hazardous Waste Generator Registration Form:

Section A - generator name and I.D. number;

Section C - generation rate;

Section D - description of generation process;

Section E - composition of waste stream;

Section N - recommended disposal or treatment method (as a check).

Using the generator rates and the compositions of the waste streams, a preliminary economic potential analysis was performed on each stream. The total amount of each component of interest for each stream was calculated on a yearly basis. This amount was then multiplied by the selling price per unit amount of that component to arrive at a component value in dollars per year. Most of the metals under study are sold in elemental form. Prices for these metals were obtained from the March 19, 1982, edition of _Iron Age_. Barium, however, is not commonly sold in elemental form and its price was not given in _Iron Age_. A brief survey of firms which market barium compounds indicated barium is frequently sold as barium sulfide which sells for approximately \$0.51/kg. This was used as the basis for the price of barium. Table 2 lists the prices of all the metals of interests used in this study. The component values for each stream were totalled to give a value of components for each stream.

Also included in the preliminary economic potential analysis is the cost of landfilling. On April 14, 1982, Browning Ferris Industries at Missouri City, Missouri reported a nation wide average cost of \$20-23/55 gallon drum to landfill solid hazardous wastes.[2] This translates to approximately \$98/m^3. This unit cost multiplied by the volume rate of generation of a waste stream in m^3/yr equals

TABLE 2

Metal Prices

Metal or Compound	Price per kg
Barium Sulfide	$ 0.51
Cadmium	3.20
Chromium	8.27
Copper	1.68
Iron	0.07
Lead	0.60
Magnesium	3.83
Mercury	11.02
Nickel	7.27
Titanium	16.53
Zinc	0.93

the yearly disposal cost to landfill a waste stream. This disposal cost was added to the total value of components to give a total stream value.

It should be noted that no transportation costs have been included. Transportation costs can easily double the cost of disposal. However, unless an alternate disposal method can be implemented at the generating facility, similar transportation cost could be incurred while using the alternate disposal method. This would result in no savings to the generator.

The total stream value provided the final basis for the decision of what streams should be investigated for possible applications of alternate disposal methods. An arbitrary limit for the total value was set at \$100,000/yr. Streams whose total values were estimated to be less than \$100,000/yr were disregarded.

Twelve streams were left after this final cut. The value of the components exceed the cost of disposal by a ratio of two to one or greater in nine of the streams. It is proposed that development of alternate disposal techniques for these streams be approached from the standpoint of separating components into salable materials. A description of these streams is presented in Table 3.

The remaining three streams are important to this study primarily because of their volume. The majority of their total value is due to their disposal costs. The approach proposed to develop alternate disposal techniques for these

TABLE 3

Streams Under Study Due to Estimated Component Value*

Stream No.	Total Value ($/yr)	Major Component	Generating Process Description
1	263,000	Cr	Solids from ferrous sulfate solution in iron oxide manufacture.
9	961,000	Zn, Hg	Dry cell battery scrap.
12	146,000	Cr	Electroplating wastewater sludge (metal hydroxides).
24	4,590,000	Fe, Pb, Zn	Electric arc furnace dust.
32	325,000	Pb	Scrap grounds incinerator residue.
39	497,000	Ba	Barium sludge from manufacture of paint pigments.
44	375,000	Ti	Waste paper and vinyl film from rotogravure printing operation.
84	6,070,000	Fe, Pb, Zn	Primary lead blast furnace slag.
95	131,000	Cr	?

*Total value of elemental components in a stream is more than twice the disposal cost.

streams is one of volume or hazard reduction. Only the hazardous components need be considered for concentration or removal. These streams are described in Table 4.

A preliminary literature survey revealed that considerable work has been devoted to recovering materials from electroplating wastewaters and from steelmaking dusts. The considerable economic data found for processes to treat these wastes suggested that these processes were at or near the commercial stage of development. Therefore, they would be technologically available at this scale. As a result, individual study estimates were conducted on stream number 12, an electroplating wastewater sludge, and stream number 24, an electric arc furnace dust, to predict the feasibility of applying a chosen recovery process to each specific stream. The predicted feasibility of the processes is based on the profitability index calculated by the discounted cash flow method. Details of the chosen processes and the study estimates are presented in the next two sections.

TABLE 4

Streams Under Study Due to Estimated Disposal Costs*

Stream No.	Total Value ($/yr)	Hazardous Components	Generating Process Description
25	979,000	Pb	Wastewater sludge from rolling brass and manufacturing ammunition.
33	213,000	Cd, Pb	Brass casting furnace refractory.
37	315,000	Cr, Pb	Waste caustic from cleaning and paint stripping.

*The major portion of the total value of the stream is due to disposal costs, not component dollar value.

III-A. RECOVERY OF METALS FROM AN ELECTRIC ARC FURNACE DUST

As presented in Table 3, stream number 24 is a metal and metal oxide dust generated by electric arc furnaces used in steelmaking. It is listed by the Missouri Department of Natural Resources as a hazardous waste in Rule 10 CSR 25-4.010(6)(H). It is designated as such by EPA hazardous waste number K061. The generator produces the dust from two shops at a reported total annual rate of 13,500 + kkg. One of the shops primarily manufactures steel ingots while the other chiefly produces steel castings. The ratio of production from the ingot shop to production from the casting shop was estimated to be between 2:1 and 3:2. It is assumed that the relative amount of dust produced in each shop is directly proportional to the relative amount of steel produced in each shop. All the dust is collected in baghouses.

As an industry average, dust is generated in electric arc furnaces at a rate of about 13 kg of dust per 1,000 kg of steel product.[3] The particle size of the dust is very fine and variable. It is not unusual that 95 percent of the dust particles have diameters less than 0.5 micron.[4] From a recycling standpoint, the small size and corresponding light weight present problems of containment in a furnace reaction zone. Most electric arc furnace dusts currently generated in this country are disposed of by landfilling.

The dust in question here is disposed of in an "on-site" landfill near the point of generation. However, this landfill does not have a permit from the EPA or the Missouri Department of Natural Resources to receive hazardous wastes. Recently, the generator has submitted an application to the EPA to develop this site as a hazardous waste landfill. If the dust were to be disposed of at the nearest hazardous waste landfill permitted to accept the waste, the estimated transportation and disposal cost would be $111/kkg,[5] or $1,500,000/yr.

Table 5 presents an analysis obtained from the generator of dust from both the ingot shop and the casting shop. This analysis deviates somewhat from that given in the Hazardous Waste Generator Registration Files. Since the analysis shown here was received directly from the generator it will be used in the rest of this study.

Taking the average ratio of ingot shop dust to casting shop dust as 7:4, the average iron concentration is 34%. Iron, being the major component, is a primary target for recovery. The average zinc concentration for the two shops is 17.6%. Economic considerations have traditionally limited oxidic feed materials for zinc recovery processes to those with zinc concentrations greater than 15%.[5] Therefore, zinc has a good recovery potential. Further, most zinc recovery processes also recover any lead that is present in the feed material. Thus, a realistic goal for metal recovery from this dust should be the ultimate reclamation of iron, zinc, and lead. The primary goal, however, is reducing the volume of the dust that is landfilled as a hazardous waste.

TABLE 5

Analysis of Stream Number 24 as Received from the Generator

Component	Percentage in Dust from: Ingot Shop	Casting Shop
Fe	33.5	34.9
Mn	3.3	3.4
Cr	0.2	0.2
SiO_2	3.9	3.4
MgO	1.4	2.7
CaO	3.4	18.0
Al_2O_3	0.4	0.5
C	0.15	0.31
S	0.3	0.32
Ni	0.03	0.02
Zn	22.0	10.0
Pb	1.83	1.01
Cu	0.3	0.19
Mo, Co, Cd, V	< 0.01	< 0.01
Na	0.65	0.40
P	0.06	0.06
F	0.3	1.0
Au	0.1	0.09
O	14.9	14.6
Other	13.3	8.9

Quantity of Ingot Shop Dust : Quantity of Casting Shop Dust
~ 1:2 to 2:3

It should be noted that the compositions of waste streams from electric arc furnaces are highly variable. One of the advantages an electric arc furnace has over some other types of furnaces used in steelmaking is its ability to produce high quality steel from scrap. The electric arc furnace allows improved control of temperature, furnace atmosphere and slag conditions. There is increased control of the refining reactions so that impurity removal can be superior and tramp elements in scrap are easier to deal with. As in any steelmaking process, the impurities that are removed come out of the process in the waste streams. Since the feed materials to an electric arc furnace are highly variable, the waste stream compositions are highly variable. For example, zinc concentrations in electric arc furnace dusts have been reported as low as 3.3%[6] and as high as 40%[7] and above.

A literature survey[5,6,8] suggested that the basic methods or recovery of metals from steelmaking dusts are:

(1) recycling the dust to iron or steelmaking furnaces;

(2) chemically leaching desired metals from the dust followed by chemical precipitation and/or electrolytic refining of those metals;

(3) roasting the dust in a reducing atmosphere to separate the dust into a volatile fraction (zinc and lead) and a nonvolative fraction (iron).

Recycling the dust to iron or steelmaking furnaces seems to be the simplest way to reclaim metals from the dust. If favorable, iron from the dust should be extracted into the melt with no appreciable reduction in product quality or equipment performance. Thus, the volume of the dust should be reduced and its concentrations of lead and zinc should increase. This would increase the value of the dust as a feed material in zinc and lead smelting.

As previously stated, one of the major problems encountered in recycling steel dusts is a result of the small particle size. If this dust is directly injected into a furnace, a large fraction will be swept away almost immediately and carried out of the furnace by flue gases. The residence time in the reaction zone will be insufficient to allow much to happen. This is especially true of electric arc furnace dusts. To avoid premature blow out, the dust can be agglomerated.

The generator of the dust presented herein has initiated a study to see if recycling this dust would be worthwhile. The method of agglomeration that has been chosen for that study is called "greenballing." The dust is mixed with water, formed into balls and then dried. Since the dust is very fine, sufficient agglomerate strength is provided by hydration of available materials in the dust (i.e., CaO).[6,8,9] So far, equipment problems not directly related to recycling have prohibited the formation of any conclusions in the generator's study.

Several agglomeration processes have been devised to produce pellets for blast furnace use. The Reclaform process uses coal-tar pitch as a binder and hardens the agglomerates by baking.[6] Lime and fine silica are added to steelmaking dusts in the MTU[6] process and the COBO[6] process. The pellets are hardened in autoclaves in both processes. Pellets formed using a portland cement binder in the Grancold[6] process are allowed to harden for three to four weeks, primarily outdoors.

As is evidenced by the above processes, the strength required for blast furnace pellets is much greater than for electric arc furnace pellets due to greater air velocities. However, blast furnaces cannot be used to smelt feed materials which have high zinc and lead content. Zinc and lead oxides and ferrites have been found to cause rapid deterioration of the refractory lining of blast furnaces.[5] The zinc and lead content of the electric arc furnace dust is sufficiently high to cause this. Therefore, this dust cannot be recycled through a blast furnace. While the pelletizing processes necessary for blast furnaces feed produce strong pellets that would work very well in electric arc furnaces, these processes are more expensive than "greenballing." In light of the workability of the greenballing process, the more complex pelletizing processes above would be unduly expensive for electric arc furnace applications.

Several hydrometallurgic processes have been developed to separate iron, lead and zinc oxides by chemical leaching. One process involves oxidizing an aqueous suspension of the dust with hydrogen peroxide, filtering, and then adding the solid residue to sufficient hydrochloric acid to form an aqueous suspension of pH=5. The solid phase in the resulting suspension is primarily an iron sludge and is removed by filtering. Zinc and lead are precipitated from the remaining liquid by adjusting the pH to 8.3 with milk of lime.[10]

Hazen Research, Inc., has patented a process for recovering zinc from steelmaking dust.[11] An aqueous solution containing a high concentration of ammonia and carbon dioxide is used to leach the dust. Metals more noble than zinc, such as lead, copper and cadmium, are precipitated from the leachate by cementing with additional zinc and the solid phase is removed by filtering. The remaining liquid is steam distilled to precipitate iron and zinc. The iron precipitates first and must be filtered out immediately. After the zinc precipitates, it is collected as the carbonate and calcined at 200 °C to 1100 °C to form zinc oxide. The zinc oxide is then washed with water to remove solubles formed in the calcining.

Amax, Inc., is developing a process called the Amax Caustic Leach - Electrowin Zinc Process.[5] At their pilot-scale electrolytic plant in Carteret, New Jersey, Amax has conducted feasibility studies using this process to extract 1,361 kg of zinc per day from high-iron zinc ore. In these studies a calcined ore was subjected to a mild reduction roast in a kiln type roaster. The leaching process was then carried out in agitated tanks using a 30% sodium hydroxide solution at 90 °C to 95 °C. The solid leach residue contained the iron from the ore and was suitable for upgrading in an electric furnace. The resulting iron could be used in steelmaking. The leachate was further purified by aerating to remove iron and cementing with zinc to remove more noble metals. Zinc is recovered from the resulting purified sodium zincate solution by electrowinning. Similar bench-scale studies have been conducted on various steelmaking wastes producing zinc recoveries of 90%.

Of the reduction roast processes that can be used to recover metal values from steelmaking wastes, the Waelz kiln process is the most widely known. The original Waelz plant in Duisburg, West Germany, was built in 1952 to recover zinc from the works' own zinc plant residues.[7] Other facilities of this type have been constructed elsewhere including the Waelz kilns at the New Jersey Zinc Company's Palmerton, Pennsylvania, facility.[5] The main component of the process is a rotary kiln. The metalbearing materials (steelmaking dust in this case), coal, limestone and excess air are fed into the kiln. The coal acts as fuel in maintaining a 1300 °C reaction temperature and as a reducing agent to produce metals from the metal oxides. The lead and zinc metals volatilize and then are reoxidized by the excess air. These oxides precipitate as dusts and are carried by the flue gases to a baghouse where they are collected. The residue remaining in the kiln contains the iron which, in the past, has been upgraded in open-arc electric furnaces. This has been discontinued due to unfavorable economics. The impure zinc oxide is the primary product. Only recently has the establishment of a market for this impure zinc oxide been reported. Prior to finding this buyer, New Jersey Zinc's Palmerton Waelz Kilns were operating at only 12.5% of capacity.

The Japanese have developed several reduction roast processes for recovering metals from steelmaking dusts generated in their country.[6] Although most of these are very similar to the Waelz kiln process, their primary goal is the recovery of iron. The lead and zinc oxide dusts that they generate are given to non-ferrous industry at no charge. Some of the manufacturers using the rotary kiln process are Kawasaki Steel, Nippon Steel, and Sumitomo.

Research done at the Rolla Metallurgy Research Center in Rolla, Missouri, suggests that shaft furnace processing to simulate a vertical retort or electrothermic furnace is the most promising approach for extracting metals from steelmaking dusts.[4] Experiments were performed on both a batch basis and a continuous basis in corresponding 4-inch shaft furnaces. A pelletized mixture of electric arc furnace flue dust and coke breeze was charged into the furnace and heated by an external source in a helium atmosphere. Operating temperatures were 1050 $^{\circ}C$ and 1100 $^{\circ}C$ in the batch furnace and 1100 $^{\circ}C$ in the continuous furnace. As no air was admitted, the lead and zinc vapors generated did not reoxidize and these metals were collected as such in a condenser. Some sodium and calcium salts were added to try to reduce the residence time necessary for processing. Ten percent NaCl additions and 10% $CaCO_3$ additions seemed to work. The continuous process produced zinc recoveries of almost 94%. The off-gas, primarily carbon monoxide, was burned.

In reexamining the processes described, the recycling efforts of the generator hold good potential for reducing the quantity of dust generated. However, some dust will continue to be generated, hopefully having increased concentrations of lead and zinc. This dust will have to be processed or disposed of.

The leaching processes are somewhat limited in their extent of recovery when applied to electric arc furnace dusts because these dust usually contain appreciable zinc ferrites.[5] Zinc ferrites will not dissolve in most leaching agents. If the zinc in these ferrites (up to 50% of the total zinc) is to be recovered the dust must be subjected to a mild reduction roast (as in the Amax process). If equipment is available for a reduction roast, why not use it to effect the separation.

Of the processes which rely solely on a reduction roast for separation of metals, those that admit oxygen to the furnace produce impure products which must be further refined. This would involve another process and a new set of costs.

The research done by the Rolla Metallurgy Research Center, however, suggests a process that would recover relatively pure iron, lead, and zinc from steelmaking dusts.

SKF Steel of Sweden has developed such a process using an electrically generated plasma to supply heat to a low shaft furnace.[12] As an excess of coke is supplied and no air is admitted, a reducing atmosphere is maintained from the furnace through the remainder of the process. Iron, lead, and zinc are recovered as metals. This is the recovery process proposed as an alternative to disposing of the electric arc furnace dust in a hazardous waste landfill. The following is a detailed study of the SKF Plasmazinc process.

III-B. THE PLASMAZINC/PLASMADUST PROCESS FOR RECOVERY OF ZINC, IRON, AND LEAD FROM WASTE OXIDE DUSTS.

The Plasmazinc and Plasmadust processes are patented processes developed by SKF Steel, Scandinavia's largest manufacturer of special steel. Both are modifications of SKF Steel's Plasmasmelt process. All are pyrometallugical reduction roast processes capable of reducing oxides of iron, zinc, lead, chromium, nickel and molybdenum to elemental metals.

The major differences among these processes are only in feed materials handling and product collection. The Plasmasmelt process allows the furnace off-gases, primarily carbon monoxide and hydrogen, to pre-reduce the oxidic feed materials. The Plasmazinc and Plasmadust processes allow for the condensation of metal vapors from these furnace gases, the condensed metals collected as products. The Plasmazinc process is designed primarily to recover zinc while the Plasmadust process is oriented toward the recovery of a variety of metals. Both are designed for particulate feed material. The Plasmazinc process will be discussed in detail.

The major units involved in the Plasmazinc process are:

(1) feed materials handling equipment;

(2) a low shaft furnace;

(3) plasma generators;

(4) a splash condenser;

(5) gas cleaning equipment;

(6) tapping and casting equipment.

Figure 2 shows a flow diagram of the Plasmazinc process.[5] Feed materials include:

(1) metal oxide dust;

(2) coal;

(3) coke;

(4) slag formers (lime, limestone, sand, etc.).

In the feed materials handling system, the oxide dust, coal and sand are slurried with water to obtain a homogenous mixture. Excess water is removed by filtering. The filter cake is then dried and crushed. The remaining slag formers are added and the mixture is fed into the low shaft furnace.

The low shaft furnace is the reaction vessel for the process. In addition to the feed mixture an excess of coke is supplied to the reactor by filling it through a hopper on its top. No air is admitted. This limits oxygen to that which is bound in the feed materials. As a result, the necessary heat for the process cannot be supplied by the combustion of the coal and coke as would be the case in most pyrometallurgical processes. Heat is supplied by injecting a small amount of recycled furnace flue gas which has been electrically excited to the ionized, or plasma, state. This plasma, along with the feed mixture, is injected through tuyeres into the lower part of the furnace. A cavity is formed in the coke here which is the reaction zone. The metal oxides in the reaction zone are reduced to elemental metals as the carbon in the coal and coke are

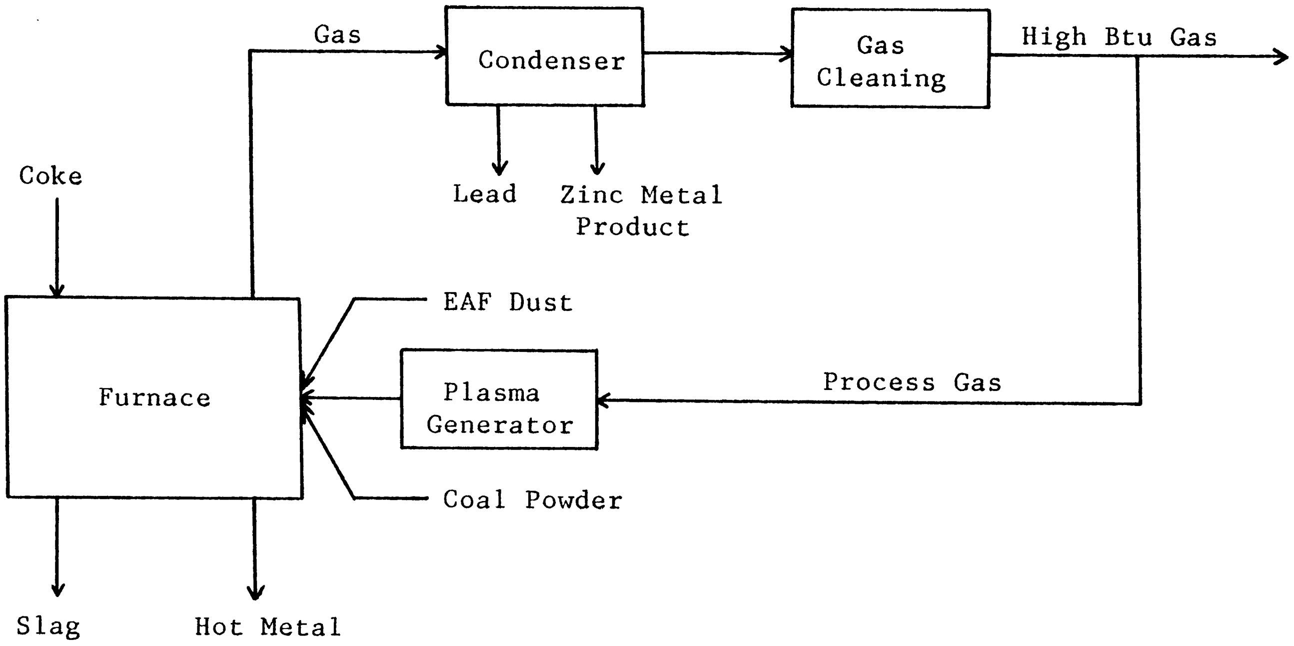


Figure 2. Flow Diagram of the Plasmazinc Process.

partially oxidized to carbon monoxide. Hydrogen bound in the coal is released predominantly as elemental hydrogen. The temperature in this reaction zone is greater than the boiling points of lead (1744 °C) or zinc (907 °C). Thus, these two metals are removed as vapor in the furnace off-gas. Metallized iron (b.p. 3000 °C) is tapped in the molten state from the bottom of the furnace. Slag is tapped separately from the bottom.

The furnace off-gas is sent through a splash condenser. Liquid lead at approximately 600 °C is sprayed on the gas. At this temperature both lead and zinc condense, the liquid zinc being highly soluble in the liquid lead.[4] This combined zinc and lead liquid is pumped to a separator bath where its temperature is reduced to slightly above the melting point of zinc (419.4 °C). At this temperature the solubility of zinc in lead is greatly decreased and the two metals separate. For example, the solubility of zinc in lead at 450 °C is only 2.15%. This is called a liquation separation process. Zinc is pulled off the top of the separator bath while the lead is withdrawn from the bottom. Part of the liquid lead (m.p. 327.5 °C) is returned to the splash condenser where the latent heat given off by the condensing vapors increases the temperature back to around 600 °C. A schematic diagram of a splash condenser is shown in Figure 3.[15]

From the splash condenser, the off-gases go to gas cleaning equipment. This rids the gas of any constituents that might make it undesirable for use as a fuel. The gaseous product is mainly carbon monoxide and hydrogen.

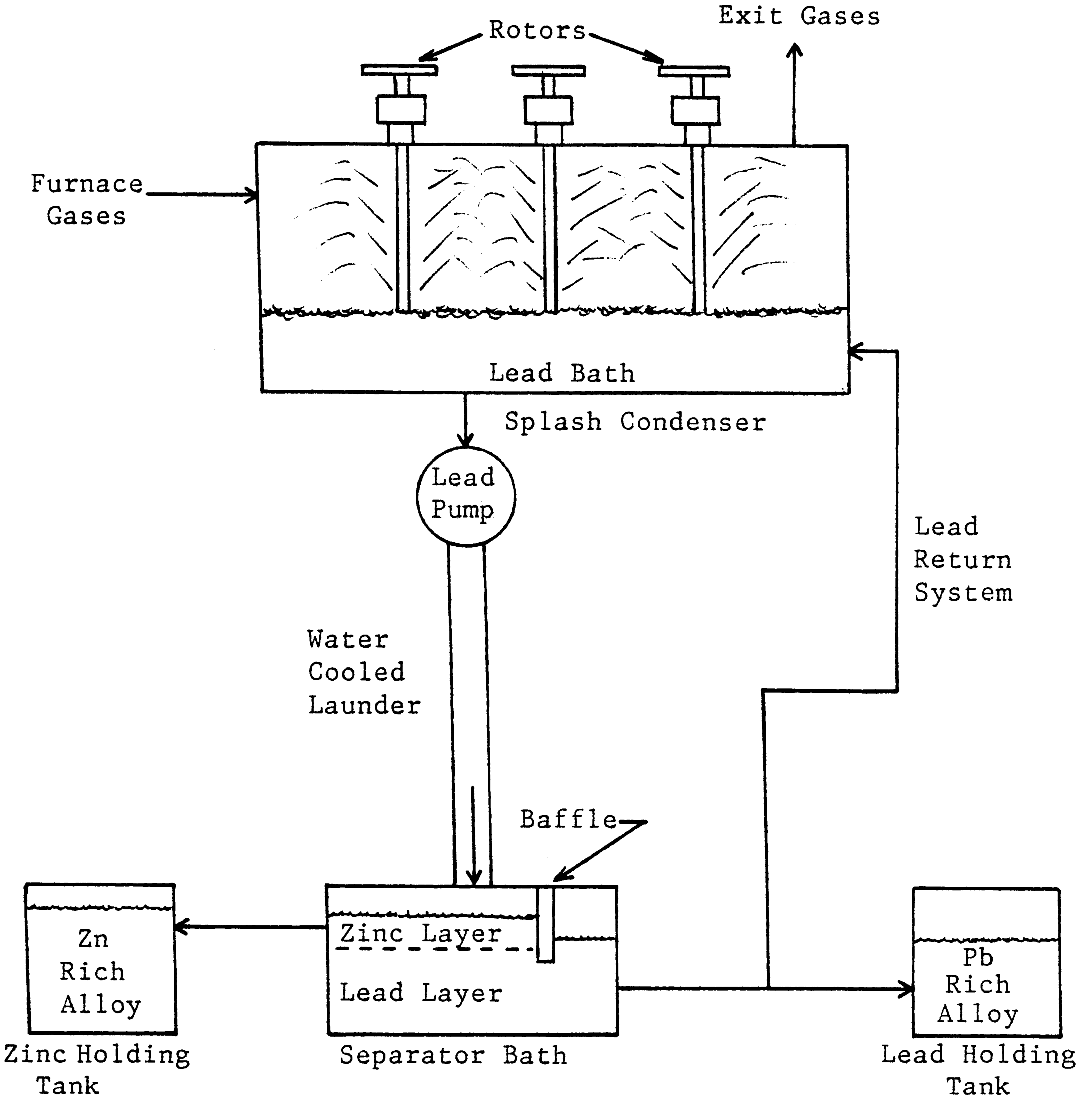


Figure 3. Schematic Diagram of a Splash Condenser.[15]

The reported heating value of this gas is 5000 kWh per kkg of fuel (coal and coke) consumed or 4300 kcal per kg of fuel consumed.

The Plasmazinc process is reported to have several advantages over other processes used for this separation. The preparation of feed materials allows that the oxide dust be placed in intimate contact with coal, a source of carbon. Similar feed preparation schemes, such as the MTU process, have shown the ability to drastically reduce the furnace residence time necessary to metallize the iron as compared to separate ore and reductant feeds.[16] Further, the plasma contains an extremely high energy concentration (between 4 and 8 kWh/m^3) so that the volume injected can be relatively small. No air is admitted resulting in the production of low volumes of gas, about 1/5 the amount produced in a blast furnace. These factors result in a relatively small equipment size being necessary for the reactor and gas handling systems. This tends to reduce capital investment. Further, the minimal gas volumes produced effect only a minimal amount of energy waste as the gases cool. This helps to offset the increased electrical energy costs as compared to the chemical energy costs of fuel used in more conventional smelting processes.

In more conventional processes where fuel is burned in air to release heat, such as the Waelz kiln process, a reducing atmosphere is maintained only near the primary combustion zone of the fuel. As the reducing gases move away from this zone they are oxidized by free oxygen. Still farther away from the primary combustion zone, oxygen is available to oxidize metal vapors, lead and zinc in this case. The lead and zinc oxides precipitate as solid particulates and can be collected as such in baghouses. But further electrothermal or carbothermal refining is required to achieve a metallized product. The exclusion of air and the provision of excess coke in the Plasmazinc process facilitate the formation of an extremely reducing atmosphere that is present throughout the system. Thus the lead and zinc are prevented from oxidizing and can be collected as elemental metals. Further refining is not required to achieve a metallized product. Also, the reducing atmosphere is composed primarily of carbon monoxide and hydrogen. This off-gas can be sold as a heating fuel.

Aside from its role in forming the reducing atmosphere, the excess coke is said to perform other duties. It is a good refractory material and therefore smoothens any temperature fluctuations in the reaction zone. The coke is also a good collector of particles in the flue gas. As the coke is consumed, the collected particles either melt or are returned to the reaction zone. This, coupled with low off-gas generation and the absence of oxide particulate production, means minimal equipment is required for gas cleaning and only a small amount of particulate matter must be disposed of.

Most of the information presented above concerning the Plasmazinc process was indirectly supplied by SKF Steel through SiAR, Inc., who are promoting the process in the U.S.A. SKF Steel obtained this information from studies of a pilot plant having a dust processing capacity of 0.4 kkg per hour. A commercial scale Plasmadust plant, which incorporates the basic technology of the Plasmazinc process, is currently being constructed at the Öresund shipyard in Landskrona, Sweden. This plant is scheduled for operation in late 1984 and will be capable of processing 70,000 kkg of dust annually.[12]

A closer look at the involved chemical reaction equilibria supports the claims of SKF Steel. The thermodynamic feasibility of a reaction depends on the free energy change for that reaction. If the free energy change is less than zero (the free energy of the products is less than the free energy of the reactants) the reaction is thermodynamically feasible. If the free energy change is greater than zero (the free energy of the reactants is less than the free energy of the products) the reaction is not thermodynamically feasible.

Figure 4 shows the standard free energy change of the pertinent oxidation reactions plotted against temperature.[14] This diagram was constructed by using the formula

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

where:

ΔG^{o} = Standard Free Energy Change for the Reaction;

ΔH^{o} = Standard Enthalpy Change for the Reaction;

ΔS^{o} = Standard Entropy Change for the Reaction;

T = Absolute Temperature.

ΔH^{o} and ΔS^{o} are not temperature independent. However, these dependencies are not strong and are such that they

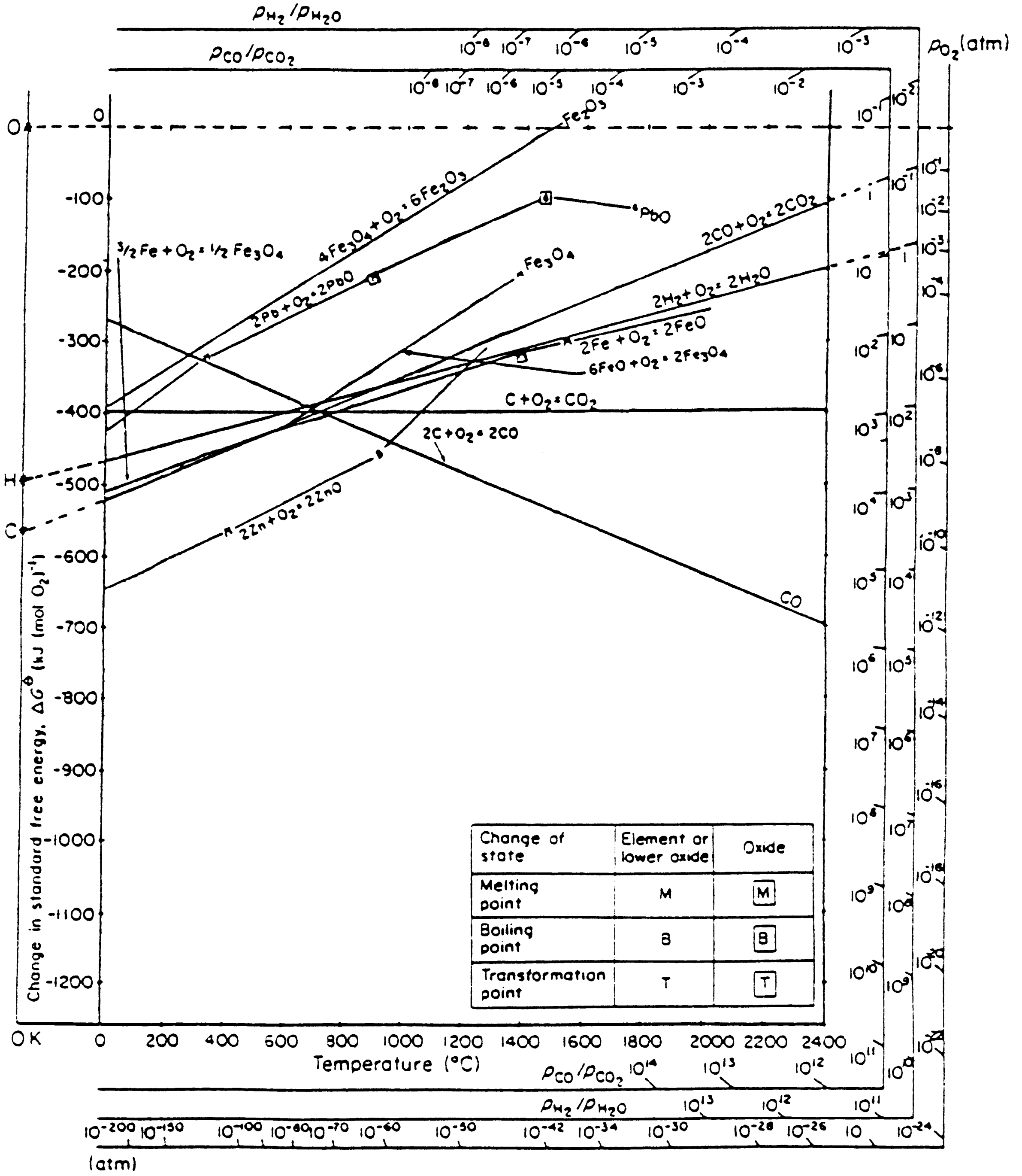


Figure 4. Change in Standard Free Energy vs. Temperature of Pertinent Oxidation Reactions.[14]

tend to cancel each other in the above equation. Thus, the temperature dependence of the standard free energy change has been treated as linear. Changes in slope (ΔS^o) occur only at transition temperatures due to phase changes.

If lead is to be kept in the vapor state, the temperature throughout the reactor must be maintained above 1744 °C, the boiling point of lead. At 2000 °C, the reaction

$$(1) \quad 2C + O_2 \rightarrow 2CO \; ; \; \Delta G^o_{2000^oC} \simeq -625 \text{ kJ/mole } O_2$$

has the most negative standard free energy change of those presented. Thus, at this temperature, carbon will reduce any of the oxides and will itself be oxidized to carbon monoxide. For example, carbon dioxide, formed at 2000 °C by the reaction

$$(2) \quad 2CO + O_2 \rightarrow 2CO_2 \; ; \; \Delta G^o_{2000^oC} \simeq -180 \text{ kJ/mole } O_2$$

will be reduced by carbon through the following reaction:

$$(3) \quad C + CO_2 \rightarrow 2CO \; ; \; \Delta G^o_{2000^oC} \simeq -220 \text{ kJ/mole C}$$

This reaction is one-half the sum of the carbon monoxide formation reaction (1) and the reverse of the carbon dioxide formation reaction (2). The standard free energy change for the reaction was calculated similarly or

$$\begin{aligned}\Delta G^o_3 &= (\Delta G_1 - \Delta G^o_2) \div (2 \text{ moles C/mole } O_2) \\ &\simeq (-625 \text{ kJ/mole } O_2 - (-180 \text{ kJ/mole } O_2)) \\ &\div (2 \text{ mole C/mole } O_2) \\ &\simeq -223 \text{ kJ/mole C.}\end{aligned}$$

Therefore, in the presence of excess carbon, the majority of the carbon dioxide formed will be reduced to carbon monoxide. The carbon will also reduce water to hydrogen at this temperature through the reaction

$$C + H_2O \rightarrow CO + H_2 \ ; \ \Delta G^o_{2000^oC} \simeq - 190 \text{ kJ/mole C.}$$

However, all of the metals and lower oxides whose oxide formation lines are above the carbon monoxide-to-carbon dioxide line ($2CO + O_2 \rightarrow CO_2$) can also be reduced by carbon monoxide through the reaction

$$CO + MO \rightarrow CO_2 + M \ ; \ M \equiv \text{Metal Atom.}$$

As this reaction occurs at a solid metal oxide-gaseous carbon monoxide interface, it is kenetically preferred to metal oxide reduction by carbon, which occurs at a solid-solid interface. The gaseous carbon dioxide generated can then be reduced by carbon back to carbon monoxide.

Table 6 lists the species of interest in order from best reducing agent to worst reducing agent at 2000 °C. Of the metals only iron is shown to be a better reducing agent than carbon monoxide. All iron (II) oxide must be reduced by carbon through the following reaction

$$C + FeO \rightarrow Fe + CO \ ; \ \Delta G^o_{2000^oC} \simeq - 180 \text{ kJ/mole C.}$$

The off-gases leave the reactor and are channeled to the condenser. Following the carbon-to-carbon monoxide line on Figure 4 in the direction of decreasing temperature, it is intersected by the zinc-to-zinc oxide line at approximately 950 °C. At this point zinc and carbon are equally

TABLE 6

Species of Interest in Order from
Best Reducing Agent to Worst Reducing Agent at 2000 °C.

Best Reducing Agent	C
	Fe
	H_2
	CO
	Pb
	FeO
	Zn
Worst Reducing Agent	Fe_3O_4

good reducing agents. At still lower temperatures, zinc becomes the better reducing agent. For example, at 907 °C, the reaction

$$Zn + CO \rightarrow ZnO + C \; ; \; \Delta G^{o}_{907\,^{o}C} \approx -50 \text{ kJ/mole C}$$

is thermodynamically feasible. 907 °C is the normal boiling point of zinc. Thus, in order to condense the zinc, the temperature must be lowered to the point that the reoxidation of zinc by carbon monoxide is feasible. Most of this reoxidation is avoided by the use of a splash condenser which provides an abrupt temperature drop. The zinc condenses and dissolves in the liquid lead cooling media before much can oxidize. Once this has happened only the zinc that contacts the liquid metal to gas interface is available for oxidation.

The remaining gases, which should consist primarily of carbon monoxide and hydrogen, leave the condenser and, after passing through the gas cleaning equipment, ultimately cool to ambient temperature. At approximately 700 °C, carbon monoxide and carbon are equally good reducing agents. Below this temperature, carbon monoxide is the better reducing agent. Below approximately 600 °C, hydrogen becomes a better reducing agent than carbon. This is obvious from Figure 4. Not so obvious is the fact that hydrogen also becomes more capable of reducing carbon monoxide than carbon monoxide is of reducing water. Below 600 °C, the hydrogen-to-water line is farther below the carbon-to-carbon dioxide line than the carbon monoxide-to-carbon dioxide line is below the hydrogen-to-water line.

For example, at 400 °C the following reactions appear to be feasible:

$CO + H_2O \rightarrow CO_2 + H_2$; $\Delta G^o_{400^oC} \cong -16.5$ kJ/mole CO

$2CO \rightarrow C + CO_2$; $\Delta G^o_{400^oC} \cong -22.5$ kJ/mole CO

$2H_2 + CO_2 \rightarrow 2H_2O + C$; $\Delta G^o_{400^oC} \cong -11.0$ kJ/mole H_2

$H_2 + CO \rightarrow H_2O + C$; $\Delta G^o_{400^oC} \cong -38.5$ kJ/mole H_2

Given the high concentrations of its reactants and its relatively large negative free energy change, the extent of the final reaction above should be much greater than the rest if the system is allowed to achieve equilibrium. This reaction is not desirable, however, from the standpoint of using the off-gas as a heating fuel. The heating value of the reacting hydrogen and carbon monoxide would be lost to form non-combustible water and solid carbon, which would precipitate out of the gas.

Fortunately this can be avoided. The rate of this reaction becomes negligible at lower (ambient) temperatures. If the hot gas can be rapidly quenched, it can be frozen in a non-equilibrium state. Thus gas cleaning equipment which induces a rapid temperature drop, such as a venturi scrubber, is recommended for this application.

The previous analysis supports SKF's claims that the products can be collected as metals and the off-gas will consist primarily of carbon monoxide and hydrogen. Using other information supplied by SKF concerning raw materials, utilities, labor and capital investment, an economic analysis for a plant capable of processing 91,000 kkg of dust annually was performed. This was reported to be minimum capacity for a Plasmazinc plant which would be economically feasible in the United States.[5] Since Missouri produces only approximately 27,300 kkg of electric arc furnace dust each year, the location of the proposed plant is Joliet, Illinois.[5] Thus, dusts from the Chicago area would be readily available.

Profitability was measured using the method of discounted cash flow rate of return. Two cases were investigated:

(1) transportation of the dust paid for by the operator of the Plasmazinc facility;

(2) transportation of the dust paid for by the generator of the dust. This transportation cost is about 53% of the estimated transportation and disposal cost to landfill the dust at the nearest permitted hazardous waste landfill.

The estimated fixed capital investment for the plant was $19,810,000. This was the same for both cases. The feasibility analysis of the first case predicted a rate of return of 4.6%. Summaries of costs and revenues for this case are presented in Tables 7 through 9. The estimated annual product cost for the second case is that for the first case less the cost of "transportation of dust." The estimated working capital for the second case is that for the first case less "1 month dust transportation cost." All other costs and revenues remain the same. The

TABLE 7

Estimated Annual Product Cost Including Dust Transportation to Process 91,000 kkg of Electric Arc Furnace Flue Dust in an Appropriately Sized Plasmazinc Process Plant - $21,550,000

I. Manufacturing Cost	$19,910,000
A. Direct Production Costs	$16,140,000
1. Raw Materials	$ 6,560,000
a. Transportation of Dust	$ 4,060,000
i. 27,300 kkg from Missouri at $59.10/kkg	$ 1,610,000
ii. 63,700 kkg from Chicago at $38.50/kkg	$ 2,450,000
b. 13,900 kkg coal at $44.00/kkg	$ 610,000
c. 3,800 kkg coke at $110.00/kkg	$ 420,000
d. Miscellaneous	$ 1,470,000
2. Operating Labor: 50 workers at $30,000	$ 1,500,000
3. Operating Supervision: 5 workers at $40,000	$ 200,000
4. Utilities: 1.4×10^8 kWh at $0.04/kWh	$ 5,600,000
5. Maintenance	$ 1,780,000
6. Operating Supplies	$ 270,000
7. Laboratory Charges	$ 230,000

TABLE 7 (con't)

Estimated Annual Product Cost Including Dust Transportation to Process 91,000 kkg of Electric Arc Furnace Flue Dust in an Appropriately Sized Plasmazinc Process Plant - $21,550,000

B. Fixed Charges	$ 1,680,000
1. Depreciation	$ 1,080,000
2. Property Taxes	$ 400,000
3. Insurance	$ 200,000
C. Plant Overhead	$ 2,090,000
II. General Expenses	$ 1,180,000
A. Administration Expenses	$ 750,000
B. Distribution and Marketing	$ 431,000
III. Research and Development	$ 460,000

TABLE 8

Estimated Working Capital Investment Including Dust Transportation for Plasmazinc Process Plant Capable of Processing 91,000 kkg of Electric Arc Furnace Flue Dust Annually - $4,260,000

I.	Raw Materials on Hand	$ 720,000
	A. 1 month dust transportation cost	$ 340,000
	B. 3 month coal supply	$ 150,000
	C. 3 month coke supply	$ 110,000
	D. 1 month supply of miscellaneous materials	$ 120,000
II.	Finished Products in Stock and Semi-finished Products in the Process of being Manufactured	$1,660.000
III.	Accounts Receivable	$1,340,000
IV.	Cash on Hand	$ 540,000

TABLE 9

Estimated Annual Revenues Generated by Plasmazinc Process Plant from 91,000 kkg of Electric Arc Furnace Flue Dust of Stream Number 24.

Product	Amount	Unit Value	Total Value
Iron	$3,095 \times 10^4$ kkg	\$234/kkg	$\$7.244 \times 10^6$
Lead	1.394×10^3 kkg	\$511/kkg	$\$0.712 \times 10^6$
Zinc	1.601×10^4 kkg	\$880/kkg	$\$14.08 \times 10^6$
Off-Gas	7.500×10^5 MWh	\$ 12/MWh	$\$0.900 \times 10^6$
		Total Revenues	$\$22.93 \times 10^6$

rate of return predicted for the second case is 15.1%. Details concerning the costs and the method of analysis are presented in Appendix A.

IV-A. REDUCTION OF THE HAZARD OF AN ELECTROPLATING WASTEWATER TREATMENT SLUDGE.

Stream number 12 is a metal hydroxide sludge resulting from treatment to remove heavy metals from an electroplating wastewater. The generating facility electroplates chromium, copper, gold, nickel, silver, and zinc. Measures taken to recover gold and silver from wastewater are fairly extensive. The remaining metals, including some impurities that leach into the solutions, such as iron and lead, are removed by hydroxide precipitation. This electroplating wastewater treatment sludge is listed by the Missouri Department of Natural Resources as a hazardous waste in Rule 10 CSR 25-4.010(6)(G). It is designated as such by EPA hazardous waste number F006.

In the wastewater treatment facility chrome (VI) is reduced to chrome (III) using sodium bisulfite. Cyanide is oxidized to carbon dioxide and nitrogen using chlorine gas. The pH of the wastewater is then adjusted to approximately 9 using lime and/or sodium hydroxide. This facilitates the formation of the insoluble metal hydroxides which precipitate. Settling of the precipitate is enhanced using polyelectrolytes. Gravity settling results in a sludge containing about 3% solids. Finally, a belt-type filter press is used to dewater the sludge to about 25% solids. This sludge is currently landfilled. The annual cost of disposal is estimated to be $60,000.

A partial analyses of four different samples of the sludge is presented in Table 10. Results of extraction procedure toxicity analyses as well as total concentrations of pertinent metals are included. The total concentrations presented deviate substantially from the metal concentrations reported in the Hazardous Waste Generator Registration Files. However, the total quantity of sludge reported in the Hazardous Waste Generator Registration Files was confirmed by the generator to be approximately 227,000 kkg/yr or 20 m^3/month.

Most of the methods that have been proposed to recover individual metals from mixed metal sludges involve liquid-liquid extraction. H. Reinhardt and H. D. Ottertun have patented a process for leaching mixed metal "slimes" and using liquid-liquid extraction to selectively extract dissolved metals from the leachate.[17] T. Clevenger proposed another liquid-liquid extraction process to reclaim metals from mixed metal electroplating rinse wastewaters. However, Clevenger noted a "severe economic limitation" in the inability of any of the chelating agents to be reused after they have been stripped of the extracted metals.[18]

Rather than trying to recover metal values from the mixed metal sludge it is possible to reduce the hazard of the sludge. Two ways of doing this are stabilizing the sludge to prevent migration (leaching) of contaminants and reducing the amounts of specific contaminants at their source, the rinsing system in this case. If the hazard

TABLE 10

Partial Analyses of Stream Number 12, An Electroplating Wastewater Treatment Sludge

Constituent	Sample 1	Sample 2	Sample 3	Sample 4
EP Toxicity				
Arsenic (mg/l)	<0.25	<0.25	<0.25	<0.25
Barium (mg/l)	<5.0	<5.0	<5.0	<5.0
Cadmium (mg/l)	0.065	0.065	0.072	0.072
Chromium (mg/l)	0.30	0.23	0.31	0.25
Lead (mg/l)	4.1	6.5	0.75	0.66
Mercury (mg/l)	<0.01	<0.01	<0.01	<0.01
Nickel (mg/l)	0.25	0.26	0.43	0.41
Selenium (mg/l)	<0.05	<0.05	<0.05	<0.05
Silver (mg/l)	<0.25	<0.25	<0.25	<0.25
Total Cadmium	2.2 mg/kg	1.8 mg/kg	2.3 mg/kg	2.3 mg/kg
Total Chromium	0.40%	0.17%	0.25%	0.26%
Chromium (VI)	1.7 mg/kg	2.1 mg/kg	0.9 mg/kg	1.9 mg/kg
Total Nickel	0.29%	0.24%	0.41%	0.43%
Free Cyanide	4.0 mg/kg	15.0 mg/kg	12.0 mg/kg	5.0 mg/kg
Complexed CN	55.0 mg/kg	40.0 mg/kg	38.0 mg/kg	49.0 mg/kg
Total Cyanide	59.0 mg/kg	55.0 mg/kg	50.0 mg/kg	54.0 mg/kg
Sampling Date	8-12-82	8-25-82	9-30-82	10-11-82
Results Reported	10-1-82	10-2-82	10-29-82	10-29-82

of a listed hazardous waste can be reduced to a level deemed nonhazardous, a regulatory exclusion of the waste from hazardous waste regulation may be granted to the generator. This can result in substantial decreases in disposal costs to the generator.

Rule 10 CSR 25-4.010(7)(A) and (7)(C) of the Missouri Department of Natural Resources describes the procedure by which individual generators may petition the department for a regulatory exclusion of their waste from hazardous waste regulation. This process is known as delisting a waste. The basis for granting a regulatory exclusion is that the specific waste, even though it is a listed hazardous waste, does not qualify as a hazardous waste under the criteria which characterize unlisted hazardous wastes. The extraction procedure toxicity test provides the unlisted hazardous waste criteria of concern here.

The intent of the extraction procedure toxicity test is to approximate the leaching tendencies of the particular waste if it were in contact with surface or groundwaters. It is used to characterize unlisted wastes as hazardous. The extraction procedure toxicity test is described in Rule 10 CSR 25-4.010(5)(B) of the Missouri Department of Natural Resources. Criteria to characterize unlisted wastes as hazardous by the extraction procedure toxicity test are presented in Table 11. If the concentration in the extraction procedure extract of any of the substances listed exceeds the level shown, the waste is classified as hazardous.

TABLE 11

Criteria for Characterizing an Unlisted Waste as an EP Toxic Hazardous Waste

EPA & M.D.N.R. Hazardous Waste Number	Contaminant	Extract Level Milligrams Per Liter
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium (VI)	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	Endrin (1,2,3,4,10,10-hexachloro-6,7 epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo,endo-5,8-dimethano naphthalene)	
D013	Lindane (1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer)	0.4
D014	Methoxychlor (1,1,1-Trichloro-2,2-bis (p-methoxyphenyl) ethane)	10.0
D015	Toxaphene($C_{10}H_{10}Cl_8$technical chlorinated camphene, 67-69 percent chlorine)	0.5
D016	2,4-D(2,4-Dichlorophenoxy-acetic acid)	10.0
D017	2,4,5-TP Silvex(2,4,5-Trichlorophenoxypropionic acid)	1.0

From the standpoint of stabilization, the metals of concern in the extraction procedure toxicity test are relatively insoluble in an alkaline environment. As pH drops, the metals become more and more soluble. Thus, one way of reducing the leachability and increasing the stability of the metals is to increase the alkalinity of their environment.

When Table 10 and Table 11 are compared, it can be seen that only sample 2 would be classified as a hazardous waste by the extraction procedure toxicity criteria (ignitable, corrosive or reactive hazardous waste criteria are not exceeded). The lead concentration of the extract from sample 2 slightly exceeded the extraction procedure toxicity criteria. In an effort to ensure that this electroplating wastewater sludge can pass the extraction procedure toxicity test, the generator has been studying the effects of adding excess lime to the sludge. It is hoped that the increased alkalinity will decrease the solubility of the relevant metals in the extraction procedure extract. Preliminary results are reported to be favorable.

Oddly enough, the metal in the sludge which is reported to be of most concern to the Environmental Protection Agency is nickel. The generator has suggested that the Environmental Protection Agency and the Missouri Department of Natural Resources have not granted a regulatory exclusion for the sludge because of its nickel levels. It is felt that the regulatory exclusion would be granted if the nickel concentration in the sludge was reduced. Thus, reducing the nickel concentration in the sludge is the goal of the process for reducing the hazard of this sludge.

The most obvious way to reduce the nickel concentration in the sludge is to reduce or eliminate its source, the nickel in the nickel plating rinse water. Further, it is desirable that the nickel be returned to the plating bath. Where evaporation from the plating bath is not excessive the nickel in the waste rinse water must be concentrated before it is returned to the plating bath. The Environmental Protection Agency has compiled data on four processes to concentrate electroplating rinse waters for return to the plating bath.[19] They are:

(1) evaporation;
(2) reverse osmosis;
(3) fixed bed ion exchange;
(4) electrodialysis.

The data presented suggests that a reverse osmosis unit would be the most economical for this application.

IV-B. THE INTEGRATED REVERSE OSMOSIS RINSE SYSTEM TO RECYCLE NICKEL PLATING CHEMICALS IN STREAM NUMBER 12

The process of reverse osmosis is used to split an aqueous stream containing a moderate concentration of solute into a high concentration stream and a low concentration stream. This is accomplished using a semipermeable membrane which allows solvent molecules to pass through while rejecting solute molecules or ions. Solvent molecules on the concentrate side of the membrane are forced through it to the dilute permeate side. The total pressure drop across the membrane must be greater than the osmotic pressure between the solutions at the interfaces on opposite sides of the membrane for this movement to occur. The pressure supplied is normally about 55 atm.[19]

In the case of the proposed integrated reverse osmosis rinse system, the concentrate stream is to be returned to the plating baths and the dilute permeate stream is to be recycled to the rinse tanks. Since the existing rinse system is to be used, one limitation for the integrated system is the flow capacity of the existing system. Flow rates after the addition of the reverse osmosis system should be similar to what they are currently.

Further, since solute rejection in a reverse osmosis system is not 100%, the permeate being recycled to the rinse tanks contains some solute. The solute concentration of the permeate must be less than the steady state solute concentration of the rinse tank to which the permeate is added. Otherwise, either the amount of solute in the dragout on the parts leaving the rinse must be greater than that on the parts entering the rinse, which would defeat the purpose of the rinse, or the solute concentration in the tank must increase, which would violate the assumption of steady state.

The two limitations presented above describe how the design of the integrated reverse osmosis rinse system is constrained by the existing rinse system. Therefore, a knowledge of existing flowrates and concentrations is needed to design the integrated system. Unfortunately, information such as dragout rates, intertank flowrates, and solute concentrations in every individual tank was not available from the generator. The only data provided by the generator was as follows:

(1) approximately 19.87 m^3/month of sludge is generated each month;

(2) the averaged nickel concentration in the sludge (from Table 10) is 0.34%;

(3) there are four nickel plating baths;

(4) the composition of the plating bath solution is:

   a. 225 g/l $NiSO_4$;

   b. 60 g/l $NiCl_2 \cdot 6H_2O$;

   c. 37.5 g/l boric acid;

(5) the operating temperature of the plating bath is 54 ^oC;

(6) the rinsing system uses a series of three tanks in a countercurrent flow arrangement;

(7) all tanks have the same volume and the same surface area of 0.37 m^2.

In order to estimate the flowrates and concentrations in the existing rinse system the following basis and assumptions were proposed:

(1) the solute concentration in the final tank is 1.872×10^{-2} g/l (2.5×10^{-2} oz/gal, one-half the final rinse concentration required for nickel plating proposed by Graham[20]);

(2) the rinse water added to the system into the third rinse has a solute concentration of zero;

(3) the water in the rinse tanks is at ambient temperature;

(4) the specific gravity of the sludge is 1.0;

(5) all of the nickel in the wastewater sludge is a result of solute in dragout on the plated parts being washed into the rinse tanks;

(6) the rinse tanks behave as ideal continuously stirred tanks;

(7) the dragout rate out of each tank is the same;

(8) the system operates at steady state;

(9) overnight and other extended period evaporative losses from tanks are replaced by batch additions of water to each tank at the start of each working day;

(10) the system is in operation 2000 hours/yr (250 days/yr, 2 shifts/day, 8 hours/shift, 1 hour operation/2 hours).

Using the above information the waste rinse water flowrate was estimated to be 2.021×10^5 l/yr. Also, the dragout flowrate was estimated to be 8.093×10^3 l/yr and the solute concentrations in the first and second rinse tanks were estimated to be 1.199×10^1 g/l and 4.840×10^{-1} g/l, respectively. Details of these calculations are presented in Appendix B.

Using different flow configurations for the integrated system, preliminary calculations were performed to give first estimates of the flowrate and solute concentration of the permeate. The concentrations and dragout flowrate estimated for the existing three tank system were used for these calculations. It was assumed that the reverse osmosis unit had a rejection rate of 98.5%.[19] To arrive at a lower limit for the permeate flowrate, the existing concentration of the (permeate) receiving rinse tank was taken as the concentration of the permeate. Results of those calculations suggested that in order to dilute the solute in the permeate to a level that could be admitted into the third rinse tank, the flow of rinse water through the tanks would have to be much greater than it is currently without recycling. This would require a membrane surface area much greater than that for a system with a higher permeate concentration. Further, substantial changes might have to be made in the rinse system piping.

However, the preliminary calculations suggested that the permeate could be recycled to the second rinse with little change in existing flowrates. The third rinse would then be independent of the remainder of the rinsing system. Control of the water flowrate through this independent rinse would allow direct control of the final "degree" to which parts are rinsed. As its required solute concentration of 1.872×10^{-2} g/l is very low compared to the rest of the system, waste rinse water from the third rinse could be used as make-up water for the rest of the rinse system. The remainder of the waste rinse water from the third rinse would contain very little nickel and could be disposed of through the existing wastewater treatment system. If the concentration of the second rinse were the same with the reverse osmosis system as without, the required rinse water flowrate would also remain the same.

More detailed calculations, which included evaporative losses and solutions added to the system to replace lost solute, confirmed that such a system could be installed with only minor changes in the rinse water flowrates. Details of these calculations are presented in Appendix B. A schematic diagram of the integrated system is shown in Figure 5.

As calculated, the reverse osmosis unit would have to process 2.372×10^{5} l/yr of rinse water having a solute concentration of 1.021×10^{1} g/l. 2.261×10^{5} l/yr of permeate with a solute concentration of 1.607×10^{-1} g/l

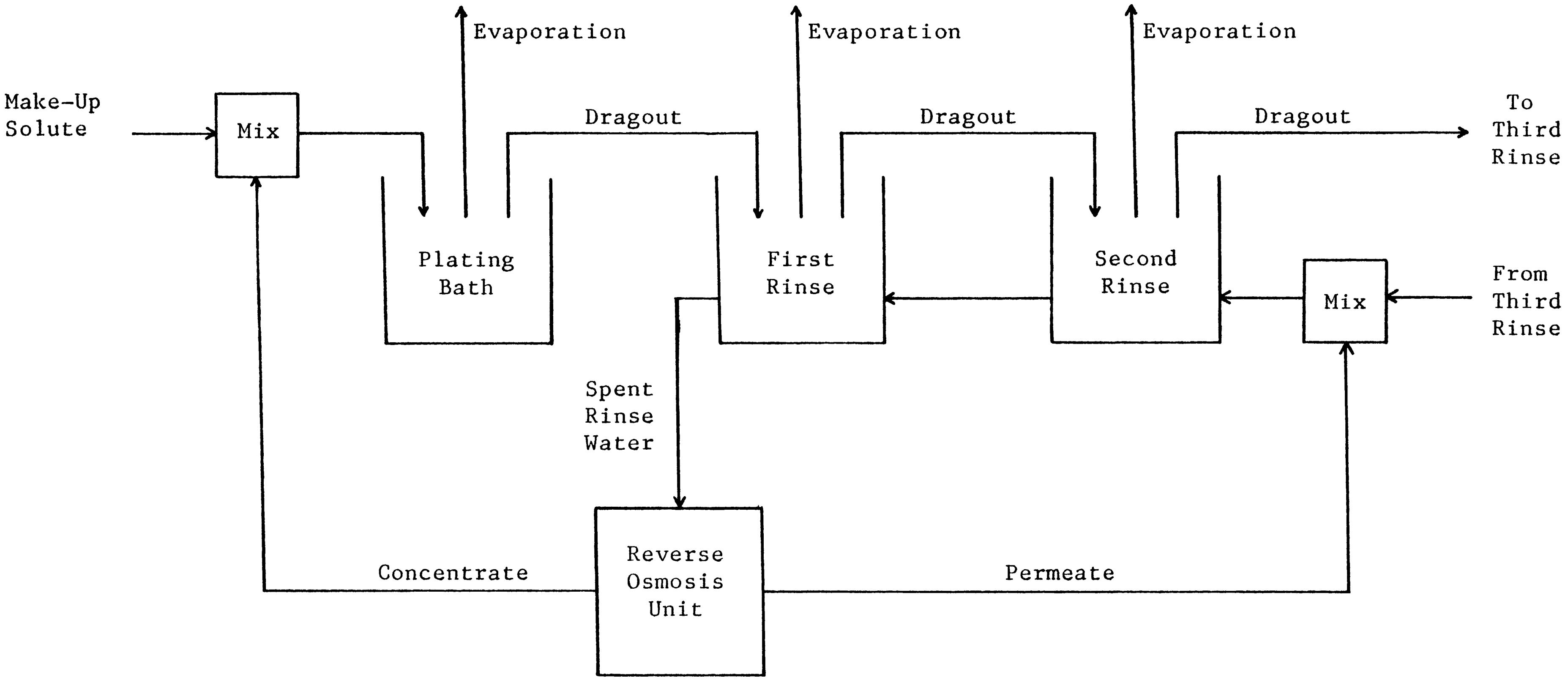


Figure 5. Schematic Diagram of the Proposed Integrated Reverse Osmosis Rinse System.

would be recycled to the rinse system. 1.109×10^4 l/yr of concentrate with a solute concentration of 2.151×10^2 g/l would be returned to the plating baths.

The third rinse would supply the system with 1.299×10^4 l/yr of make-up water having a solute concentration of 1.872×10^{-2} g/l. The remainder of the waste water from the third rinse, 2.011×10^5 l/yr, would contain only 1.278×10^3 g of nickel that would have to be disposed of each year. The amount of nickel currently disposed of in the wastewater treatment sludge is estimated to be 2.291×10^6 g/yr. Thus, it is estimated that the integrated reverse osmosis rinse system could reduce the amount of nickel in the wastewater sludge by over 99.9%. It is assumed that this reduction in nickel would be sufficient to induce the Environmental Protection Agency to grant a regulatory exclusion of this waste from hazardous waste regulation.

From permeate flux rate data presented by the Environmental Protection Agency,[19] the reverse osmosis membrane area required would be approximately 16.0 m^2. This is about half the minimum size unit commercially available. Thus, costs were based on this minimum size unit having a membrane area of about 32.5 m^2 and a 1979 cost of approximately $15,000. A summary of costs and savings are presented in Tables 12 through 14. Any 1979 costs used were scaled to December, 1982 costs using CE plant cost indices.[21] The projected savings to the generator were primarily the result of projected decreases in sludge disposal costs. These

TABLE 12

Summary of Estimated Total Investment for Proposed Reverse Osmosis System (1982 Cost) - $65,200

I.	Fixed Capital Investment	$52,200
	A. Direct Cost	$32,900
	1. Equipment	$27,600
	a. Reverse osmosis unit w/50 μm filter and centrifugal pump	$19,700
	b. Activated carbon filter	$ 2,600
	c. Piping	$ 3,300
	d. Miscellaneous	$ 2,000
	2. Installation labor and materials	$ 5,300
	a. Site preparation	$ 300
	b. Plumbing	$ 3,300
	c. Electrical	$ 700
	d. Miscellaneous	$ 1,000
	B. Indirect Cost	$14,700
	1. Engineering and supervision	$ 9,700
	2. Construction expense	$ 3,300
	3. Contractors fee	$ 1,700
	C. Contingency	$ 4,500
II.	Working Capital Investment	$13,000

TABLE 13

Summary of Estimated Annual Cost of Operation for Proposed Reverse Osmosis System (1982 Cost) - $19,110

I.	Annual operating costs	$11,020
	A. Labor: 100 hr/yr @ $15/hr	$ 1,500
	B. Maintenance and operating supplies: 12.65% of fixed capital investment	$ 6,600
	C. Plant overhead	$ 860
	D. Raw materials	$ 1,970
	1. Replacement membranes: 3/yr @ $440	$ 1,320
	2. Resin for carbon filter	$ 650
	E. Utilities: 2,000 kwh @ $0.45/kwh	$ 90
II.	Fixed costs	$ 8,090
	A. Depreciation: 10% of total investment	$ 6,520
	B. Taxes and insurance	$ 1,570

TABLE 14

Estimated Annual Savings from Integrated
Reverse Osmosis Rinse System - \$31,660

Item	Amount	Unit Value	Total Value
$NiSO_4$	4.855×10^2 kg	\$1.96/kg	\$ 950
$NiCl_2$	2.648×10^2 kg	\$2.68/kg	\$ 710
Disposal Cost	(one-half of current disposal cost)		\$30,000
		Total Savings	\$31,660

savings are dependent on the generator's procurement of a regulatory exclusion for this waste.

The feasibility of this system was analyzed using the method of discounted cash flow. Based on an expected project life of 10 years, the rate of return was estimated to be 15.8%. Details of this feasibility analysis can be found in Appendix C.

It should be noted that the recycling system will allow contaminants to build up in the plating baths. When contamination becomes excessive the plating bath solution will have to be replaced. In calculating savings from reduced chemical costs, it was assumed that the solution was replaced once each year. This reflects something of a maximum savings as replacement would probably be required more frequently. Estimation of the frequency of replacement would require information beyond the scope of this study. Suffice it to say that actual savings in plating chemical costs will be less than predicted. This should have little effect on the projected rate of return, however, due to the small contribution that chemical savings makes to total savings.

The cost of disposal of the contaminated plating bath solution should also be negligible compared to total savings. Each plating bath contains approximately 280 liters of solution. This small amount could be batch treated to precipitate metals and the sludge disposed of separately. Or, since it is concentrated, a plating chemical manufacturer might be found who could purify the contaminated solution. Some plating chemical manufacturers offer credits on future chemical purchases to generators for concentrated waste plating solutions.

V. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

The purpose of this study was to investigate the use of technologically available processes as economically feasible alternatives to land disposal of hazardous wastes. A review of categories of hazardous wastes prescribed by the Missouri Department of Natural Resources suggested that the majority of the hazardous wastes currently generated in Missouri and disposed of on or in the land are contaminated with heavy metals. Thus, the study was limited to these heavy metal contaminated streams.

Data on relevant hazardous wastes generated in Missouri were taken from the Hazardous Waste Generator Registration Files of the Missouri Department of Natural Resources. These data included the amount, composition, and generating process of the waste stream. To further limit the range of search for alternate disposal processes, a preliminary economic evaluation of each stream was performed. This involved multiplying the amount of each metal in each stream by that metal's unit market value and adding these total metal values of each stream. An estimated cost of disposal was then added to this total component value to arrive at the total estimated value of the stream. Streams with a total estimated value of less than $100,000 were disregarded.

Twelve streams have estimated total values greater than $100,000. The greater element of estimated value in nine of these streams is total component value. The estimated value of the other three streams lies primarily in disposal costs. Tables 3 and 4 present summaries of the preliminary economic potential analysis for all these streams.

A general review of literature disclosed that a considerable amount of work had been done to apply alternate processes to steelmaking waste dusts and electroplating waste rinse water. Thus, streams number 12, an electroplating waste water sludge, and number 24, an electric arc furnace steelmaking dust, were chosen for detailed study. A detailed description of a possible alternate process, including a profitability analysis by method of discounted cash flow for each of these streams was presented.

The Plasmazinc process developed by SKF Steel of Sweden was chosen to reclaim iron, lead, and zinc from the stream number 24. Using almost identical technology, a Plasmadust process plant capable of processing 70,000 kkg of dust annually is currently being built in Landskrona, Sweden. Literature supplied by SKF suggests that a Plasmazinc plant would have to be capable of processing approximately 91,000 kkg/yr of high zinc steelmaking dusts to be feasible in the United States. Missouri does not produce that much dust. Therefore, it was proposed to locate the plant in Joliet, Illinois, to receive dust from the Chicago area as well. An economic analysis was performed for two schemes of operating costs for this plant. In the first, transportation of the dust to the Plasmazinc plant was paid for by the Plasmazinc plant. The rate of return was projected to be

4.6% continuously over the 18 year life of the project. In the second scheme, transportation of the dust was paid for by the generator. In this case, the rate of return for the Plasmazinc process was projected to be 15.1%.

Stream number 12 is a listed hazardous waste under Environmental Protection Agency Hazardous Waste Number F006. As reported by the generator, attempts to delist this waste have not been accepted by the Environmental Protection Agency because of the amount of nickel in the sludge. Thus, it is proposed that a reverse osmosis unit be used to concentrate and recycle plating chemicals in the nickel plating line. By recycling the concentrate to the plating baths and the permeate to the second rinse in a series of three countercurrent rinses, nickel discharged from the nickel plating line could be reduced by over 99.9%. If the resulting wastewater treatment sludge could be delisted, it is assumed that disposal costs could be cut in half. This savings, along with savings from reduced plating chemical usage, would effect a continuous rate of return of 15.8% over the 10 year service life. Not taken into account here is the periodic dumping of the plating baths that will be required to remove built up contaminants.

Conclusions

Based on this study, the Plasmazinc process could be used to economically recover iron, lead, and zinc from stream number 24 and an integrated reverse osmosis rinse system could be used to economically recycle nickel plating chemicals that currently contaminate stream number 12. In the case of the Plasmazinc process, the waste generator would have to pay the cost of transporting the dust to the recovery facility. The projected transportation cost would be only about 53% of the estimated cost of transportation and disposal at Bob's Home Service hazardous waste landfill in Wright City, Missouri.

The integrated reverse osmosis rinse system prescribed for stream number 12 would be potentially feasible only if the electroplating wastewater sludge could be delisted. If the electroplating wastewater sludge could not be delisted, the savings incurred by reducing chemical usage appears to be insufficient to pay for the project in this case.

The elimination of these two streams from hazardous waste land disposal would reduce the total mass of hazardous waste generated in Missouri and disposed of on or in the land by approximately 10%.

Recommendations

As defined by Peters and Timmerhaus,[22] the cost estimates presented are "study estimates." As such, the probable accuracies are ± 30%. More detailed cost studies should be performed to improve the accuracies of the predicted rates of return. The generators have ready access to information of a precision beyond the scope of this study which could greatly affect the predicted rates of return. This information includes what affects the generator's recycling efforts will have on stream number 24 and how frequently the plating bath related to stream number 12 will have to be replaced. Ultimate decisions of feasibility should be based on these detailed studies.

In view of its many modifications, the basic technology of the Plasmazinc process appears to be very versatile. While the total amount of steelmaking dusts generated annually in Missouri is estimated to be only 27,300 kkg, other kinds of wastes streams could possibly serve as feed material to this process. Stream number 32 contains 355 kkg/yr lead. Stream number 84 contains 11,700 kkg/yr iron, 650 kkg/yr lead, and 3700 kkg/yr zinc. While the estimated unit value of these streams is on the order of half that of stream number 24, a modification of the Plasmazinc process might be able to economically extract metals from these wastes. If this were the case, it might be advantageous to locate the recovery facility closer to or in Missouri. Thus, Missouri generators would have to pay less for transportation. These possibilities should be investigated. Elimination of these streams from land disposal would amount to a 37% reduction in land disposed hazardous waste.

The analyses of processes presented herein show those processes to be economically advantageous to the generator. Economic considerations must weigh heavily in our decisions regarding hazardous waste disposal. The consumer is the one who ultimately pays for environmental protection. If industry is forced to use waste disposal methods which increase costs, the consumer will have to pay more for products, pay more taxes for subsidies, or tolerate a loss of jobs and products. Unrealistic restrictions on waste disposal can be excessively costly. However, restrictions which are insufficient to prevent the inadvertent contamination of our environment with hazardous materials can also be excessively costly. These costs include clean up costs as well as the invaluable costs of life and health. We must continue to develop economically sound and technically efficient alternatives to land disposal of hazardous wastes so that fewer restrictions can be deemed unrealistic.

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APPENDIX A

Calculation of Discounted Cash Flow Rate of Return for 91,000 kkg/yr Plasmazinc Plant

To project the discounted cash flow rate of return, the following parameters must be estimated as functions of time:

(1) fixed capital investment;
(2) non-depreciable items of fixed capital investment (land);
(3) working capital investment;
(4) cash flow after plant startup.

For this study, it is assumed that the land for the plant is purchased one year prior to startup and the fixed capital investment other than for land is made continuously and at a constant rate throughout a construction period of one year. The working capital investment is then supplied at the time of plant startup (time zero).

To estimate the cash flow after plant startup, the following additional information must be estimated as functions of time:

(1) revenues;
(2) total product cost;
(3) taxes;
(4) depreciation.

Prior to startup, the values of these items are assumed to be zero. After startup, they are assumed to be continuous and constant with respect to time.

Unfortunately, some of the cost data used herein was not obtained in its most convenient form. For example, literature from SKF Steel supplied an estimate of the total investment for the project rather than individual fixed capital and working capital investment figures. It was necessary to estimate the working capital investment and subtract that from the total investment to arrive at the estimated fixed capital investment. However, the estimation of the working capital investment required a knowledge of total product cost which was estimated in terms of fixed capital investment. This is noted here in anticipation of any confusion that might arise as a result of the apparent disorder in the following sequence of calculations.

The following calculations are based on a Plasmazinc process plant capable of processing 91,000 kkg of electric arc furnace flue dust. This electric arc furnace dust is assumed to have the same composition as stream number 24. An averaged ratio of shop #1 dust to shop #2 dust of 7 to 4 is used to arrive at the average concentrations presented in Table 15. The proposed plant is to be constructed in Joliet, Illinois.

The estimated total product cost as a function of the fixed capital investment for this plant is presented in Table 16. The amount of electricity required was estimated using the data supplied by SKF Steel presented in Table 17. Other feed material quantities as well as the required quantity of labor, were also supplied by SKF Steel.

TABLE 15

Average Concentrations of Iron, Lead, and Zinc in Stream Number 24

Component	Concentration
Iron	34.0%
Lead	1.53%
Zinc	17.6%

TABLE 16

Estimated Annual Product Cost[22] to Process
91,000 kkg of Electric Arc Furnace Flue Dust
in an Appropriately Sized Plasmazinc Process Plant
- &16,650,000 + 24.71% of Fixed Capital Investment

I. Manufacturing Cost - $14,220,000 + 24.22% of fixed capital investment

A. Direct Production Costs: $14,090,000 + 10.35% of fixed capital investment

1. Raw Materials	$6,560,000
a. Transportation of Dust	$4,060,000
i. 27,300 kkg from Missouri at $59.10/kkg[5]	$1,610,000
ii. 63,700 kkg from Chicago at $38.50/kkg	$2,450,000
b. 13,900 kkg[13] coal at $44.00/kkg	$ 610,000
c. 3,800 kkg[13] coke at $110.00/kkg	$ 420,000
d. Miscellaneous[13]	$1,470,000
2. Operating Labor: 50 workers[13] at $30,000	$1,500,000
3. Operating Supervision: 5 workers[13] at $40,000	$ 200,000
4. Utilities: 1.4×10^8 kwh at $0.04/kwh[23]	$5,600,000
5. Maintenance: 9% of fixed capital investment	
6. Operating Supplies: 15% of maintenance cost = 1.35% of fixed capital investment	
7. Laboratory Charges: 15% of operating labor = $230,000	

TABLE 16 (con't)

Estimated Annual Product Cost[22] to Process
91,000 kkg of Electric Arc Furnace Flue Dust
in an Appropriately Sized Plasmazinc Process Plant
- $16,650,000 + 24.71% of Fixed Capital Investment

B. Fixed Charges: 8.4% of fixed capital investment

1. Depreciation: 5.47% of fixed capital investment
2. Property Taxes: 2% of fixed capital investment
3. Insurance: 1.0% of fixed capital investment

C. Plant Overhead: 60% of operating labor, supervision and maintenance = $1,020,000 + 5.4% of fixed capital investment

II. General Expenses - $750,000 + 2% of total product cost

A. Administration Expenses: 50% of operating labor = $750,000

B. Distribution and Marketing: 2% of total product cost

III. Research and Development - 2% of total sales = $460,000

TABLE 17

Energy Requirements for Plasmazinc Plant

Metal	Amount (kkg)	Unit Energy Requirement[13] (kWh)	Total Energy Requirement (kWh)
Zinc	1.601×10^4	2530	40.48×10^6
Lead	1.394×10^3	604	0.842×10^6
Iron	3.095×10^4	2360	73.10×10^6
Other	4.265×10^4	604	25.78×10^6
	Total Energy Required		140.2×10^6 kWh

Depreciation was calculated using the straight line method over an estimated equipment life of 18 years and a zero salvage value. Land, with an estimated value of 1.5% of the fixed capital investment, was not included in the depreciation. The remaining cost factors were taken from Peters and Timmerhaus.[22]

Working capital consists of the amount of money needed to provide for:

(1) raw materials and supplies carried in stock;
(2) finished products in stock and semifinished products in the process of being manufactured;
(3) accounts receivable;
(4) cash kept on hand for monthly payment of operating expenses;
(5) accounts payable;
(6) taxes payable.

Raw materials on hand can usually be valued at one month's supply. Coal, however, is produced on the average of only 230 days per year.[23] Therefore, provisions must be made for a 3 month supply. Finished products in stock and semifinished product values can be estimated as the total manufacturing cost for one month of production. Accounts receivable from customers are normally based on a 30 day allowable payment period. Thus, the approximate amount of working capital that must be apportioned to accounts receivable is one month's production cost. Cash kept on hand should amount to the sum of one pay period's labor and supervision cost and one month of utilities costs. A summary of the estimated working capital investment is presented in Table 18. While entries for accounts payable and taxes payable are not included, the ratio of working capital to fixed capital projected here compares favorably to that predicted by Peters and Timmerhaus.[22]

The total investment for the plant was estimated by SKF Steel to be \$20,000,000 in 1980.[13] The annual CE plant cost index for 1980 is 261.2. The CE plant cost index for December, 1982, is 314.3.[21] Thus the necessary total investment in December, 1982, would have been:

$$\$20{,}000{,}000 \quad \left(\frac{314.3}{261.2} \right) = \$24{,}070{,}000$$

The total investment is the sum of the fixed capital investment and the working capital investment. As the total investment and the working capital investment are known, the fixed capital investment can be calculated:

$$F = T.I. - W$$

where

F = fixed capital investment

$T.I.$ = total investment

W = working capital investment

or,

$$F = \$24{,}070{,}000 - (\$3{,}690{,}000 + .0288F)$$

$$1.0288F = \$20{,}380{,}000$$

$$F = \$19{,}810{,}000$$

and,

$$W = \$3{,}690{,}000 + .0288F$$

$$= \$4{,}260{,}000.$$

TABLE 18

Estimated Working Capital Investment[22] for Plasmazinc Process Plant Capable of Processing 91,000 kkg of Electric Arc Furnace Flue Dust Annually - $3,690,000 + 2.88% of Fixed Capital Invesment

I.	Raw Materials on Hand	$720,000
	A. 1 month dust transportation cost.	$340,000
	B. 3 month coal supply	$150,000
	C. 3 month coke supply	$110,000
	D. 1 month supply of miscellaneous materials	$120,000
II.	Finished Products in Stock and Semifinished Products in the Process of Being Manufactured - 1 month manufacturing cost = $1,260,000 + 2.02% of fixed capital investment	
III.	Accounts Receivable - 1 month direct production cost = $1,170,000 + 0.86% of fixed capital investment	
IV.	Cash on Hand - 1 beweekly payroll period cost + 1 month utility cost = $540,000	

Also,

$E = \$16,650,000 + .2471F$

$= \$21,550,000$

$D = .0547F$

$= \$1,080,000$

where:

E = annual total product cost;

D = annual depreciation.

Revenues from the sale of the recovered metals and the off-gas are presented in Table 19 along with the amounts and unit selling prices of each item. Taxes on corporate income amount to approximately 27% of the first $100,000 income plus 46% of all income over $100,000. Using these values along with the estimates for total product cost and depreciation, the cash flow after startup can be calculated as follows:

$I = S - E$

$= \$22,930,000 - \$21,550,000$

$= \$1,380,000$

$T = 0.46\ (I - \$100,000) + 0.27\ (\$100,000)$

$= 0.46\ (\$1,280,000) + 0.27\ (\$100,000)$

$= \$620,000$

$P = I - T$

$= \$1,380,000 - \$620,000$

$= \$760,000$

$C = P + D$

$= \$760,000 + \$1,080,000$

$= \$1,840,000$

TABLE 19

Estimated Annual Revenues Generated by Plasmazinc Process Plant from 91,000 kkg of Electric Arc Furnace Flue Dust of Stream Number 24

Product	Amount	Unit Value[24]	Total Value
Iron	3.095×10^4 kkg	\$234/kkg	\$7.244 x 10^6
Lead	1.394×10^3 kkg	\$511/kkg	\$0.712 x 10^6
Zinc	1.601×10^4 kkg	\$880/kkg	\$14.08 x 10^6
Off-Gas	7.500×10^4 MWh	\$ 12/MWh	\$0.900 x 10^6
		Total Revenues	\$22.93 x 10^6

where

I = annual income

T = annual taxes

P = annual profits

S = annual revenues

C = annual cash flow

At time zero (plant startup) the value of the land which was purchased one year prior to startup is equal to:

$$\begin{aligned} L &= .015Fe^r \\ &= .015\ (\$19{,}810{,}000)\ e^r \\ &= 300{,}000\ e^r \end{aligned}$$

where

L = compounded land value at time zero

r = discounted cash flow rate of return

The construction cost is the fixed capital investment less the cost of the land. This cost was incurred continuously and at a constant rate throughout the one year construction period prior to plant startup. The time zero value of the constuction cost is:

$$\begin{aligned} B &= (F - .015F)(e^r-1)/r \\ &= \$19{,}510{,}000\ (e^r-1)/r \end{aligned}$$

where

B = the compounded construction cost.

The working capital is supplied at time zero and, therefore, is not compounded here;

$$W = \$4{,}260{,}000$$

Thus the cash position at time zero is:

$$\begin{aligned} CP_{zero} &= L + B + W \\ &= \$300{,}000\ e^{r} + \$19{,}510{,}000\ (e^{r}-1)/r + \$4{,}260{,}000 \end{aligned}$$

The cash flow to the project is assumed continuous and constant each year. Further, the annual cash flow is the same each year. The time zero value of the cash flow compounded over the 18 years from plant startup to the end of the project is:

$$\begin{aligned} CF_{zero} &= C\ \left(\frac{e^{18r}-1}{re^{18r}} \right) \\ &= \$1{,}840{,}000\ (e^{18r}-1)/re^{18r} \end{aligned}$$

When the project is completed, the land cost and the working capital can be recovered. The time zero value of these monies is:

$$\begin{aligned} WL_{zero} &= (L + W)/e^{18r} \\ &= \$4{,}560{,}000/e^{18r} \end{aligned}$$

To break even, the value of the money paid out must equal the value of the money recovered. Thus the rate of return, r, must be found such that:

$$CP_{zero} = CF_{zero} + WL_{zero}$$

A trial and error approach was used to find r which in this case is 4.6%.

The calculations presented above were for the case which included the cost of transporting the dust in the recovery facilities costs. Subtracting the dust transportation cost from the total product cost, the total product cost without transportation is:

$$\begin{aligned} E &= \$21{,}550{,}000 - \$4{,}060{,}000 \\ &= \$17{,}490{,}000 \end{aligned}$$

In this case, no working capital is needed for the one month supply of dust. Therefore:

$$W = \$4{,}260{,}000 - \$340{,}000$$
$$= \$3{,}920{,}000$$

The land cost, the fixed capital investment, and revenues remain the same. Cash flow is calculated as follows:

$$I = S - E$$
$$= \$22{,}930{,}000 - \$17{,}490{,}000$$
$$= \$5{,}440{,}000$$
$$T = 0.46\ (I - \$100{,}000) + 0.27\ (\$100{,}000)$$
$$= 0.46\ (5{,}340{,}000) + (100{,}000)$$
$$= \$2{,}480{,}000$$
$$P = I - T$$
$$= \$5{,}440{,}000 - \$2{,}480{,}000$$
$$= \$2{,}960{,}000$$
$$C = P + D$$
$$= \$2{,}960{,}000 + \$1{,}080{,}000$$
$$= \$4{,}040{,}000$$

The cash position at time zero is:

$$CP_{zero} = L + B + W$$
$$= \$300{,}000\ e^{r} + 19{,}510{,}000\ (e^{r}-1)/r + \$3{,}920{,}000$$

The time zero value of the cash flow after plant startup is:

$$CF_{zero} = C\ (e^{18r}-1)/re^{18r}$$
$$= \$4{,}040{,}000\ (e^{18r}-1)/re^{18r}$$

The time zero value of the capital recovered at the end of the project from land and working capital is:

$$WL_{zero} = (L + W)/e^{18r}$$

$$= 4{,}220{,}000/e^{18r}$$

setting:

$$CP_{zero} = CF_{zero} = + WL_{zero}$$

and solving for r by trial and error, the rate of return for this case was found to be 15.1%.

It has been estimated that the cost of transporting and disposing of the dust at Bob's Home Service to be \$111/kkg.[5] Thus, the cost of transporting the dust to the proposed Plasmazinc plant of \$59.10/kkg is about 53% of the total cost of disposal in this permitted hazardous waste landfill.

APPENDIX B

Design of the Reverse Osmosis System to Recycle Nickel Plating Solute from Stream Number 12

The nickel in stream number 12 originates from a nickel electroplating bath and rinse system. The rinse system consists of a series of three interconnected rinse tanks. Rinse water flows through the system in the direction countercurrent to the direction of "flow" of the parts that are being rinsed. If no modifications of the existing system are to be needed for its use in the integrated reverse osmosis rinse system, flow parameters through the rinse system need to be similar before and after the reverse osmosis unit is added. Therefore, the existing flow parameters are estimated first in the following sequence of calculations.

The design of the integrated reverse osmosis rinse system is based on an annual operating time of 2,000 hours. This same basis is assumed for the existing system. Data obtained from the generator concerning stream number 12 and the nickel plating line is as follows:

(1) approximately 20 m^3 of sludge are generated each month;

(2) the averaged nickel concentration in the sludge (from Table 10) is 0.34%;

(3) there are four nickel plating baths;

(4) the composition of the plating bath solution is:

   a. 225 g/l $NiSO_4$;
   b. 60 g/l $NiCl_2 \cdot 6H_2O$;
   c. 37.5 g/l boric acid;

(5) the operational temperature of the plating baths is 54 °C;

(6) the rinsing system uses a series of three tanks in a countercurrent flow arrangement;

(7) all tanks have the same volume and the same surface area of 0.37 m^2.

The following assumptions were made:

(1) the solute concentration in the final tank is 1.872×10^{-2} g/l (2.5×10^{-2} oz/gal., one half the final rinse concentration required for nickel plating proposed by Graham[20]);

(2) the rinse water added to the system into the third rinse has a solute concentration of zero;

(3) the rinse water is at ambient temperature;

(4) the specific gravity of the sludge is 1.0;

(5) all of the nickel in the wastewater sludge is a result of solute in dragout on the plated parts being washed into the rinse tanks;

(6) the rinse tanks behave as ideal continuously stirred tanks;

(7) the dragout rate out of each tank is the same;

(8) the system operates at steady state;

(9) overnight and other extended period evaporative

losses from tanks are replaced by batch additions of water to each tank at the start of each working day.

Figure 6 is a schematic diagram of the rinse system showing the variables used in the following calculations.

The amount of solute in the plating bath is the sum of the amounts of $NiSO_4$, $NiCl_2$, and boric acid. The $NiCl_2$ is added to the bath as $NiCl_2 \cdot 6H_2O$. The percentage of $NiCl_2$ in $NiCl_2 \cdot 6H_2O$ is 54.53%. Thus the solute concentration in the plating bath is:

$$X_D = 225 \text{ g/l} + (.5453)(60) \text{ g/l} + 37.5 \text{ g/l}$$
$$= 295.2 \text{ g/l}$$

The total amount of nickel in stream number 12 is:

$$(19.87 \text{ m}^3\text{/month})(12 \text{ month/yr})$$
$$\times (.0034 \text{ g Ni/g sludge})(1 \times 10^6 \text{ g/m}^3)$$
$$= 8.107 \times 10^5 \text{ g/yr.}$$

The percentage of nickel in the plating bath solute is 33.93%. Thus the solute passing through the system is

$$S_1 = \frac{8.107 \times 10^5 \text{ g Ni/yr}}{.3393 \text{ g Ni/g solute}}$$
$$= 2.389 \times 10^6 \cdot \text{g/yr}$$

An overall solute mass balance on the system is

$$DX_D = (F-3E_R)\, X_1 + DX_3$$

but

$$(F-3E_R)\, X_1 = S_1$$

so

$$D = \frac{S_1}{(X_D-X_3)} = \frac{2.386 \times 10^6 \text{ g/yr}}{(292.2 \text{ g/l} - 1.872 \times 10^{-2} \text{ g/l})}$$

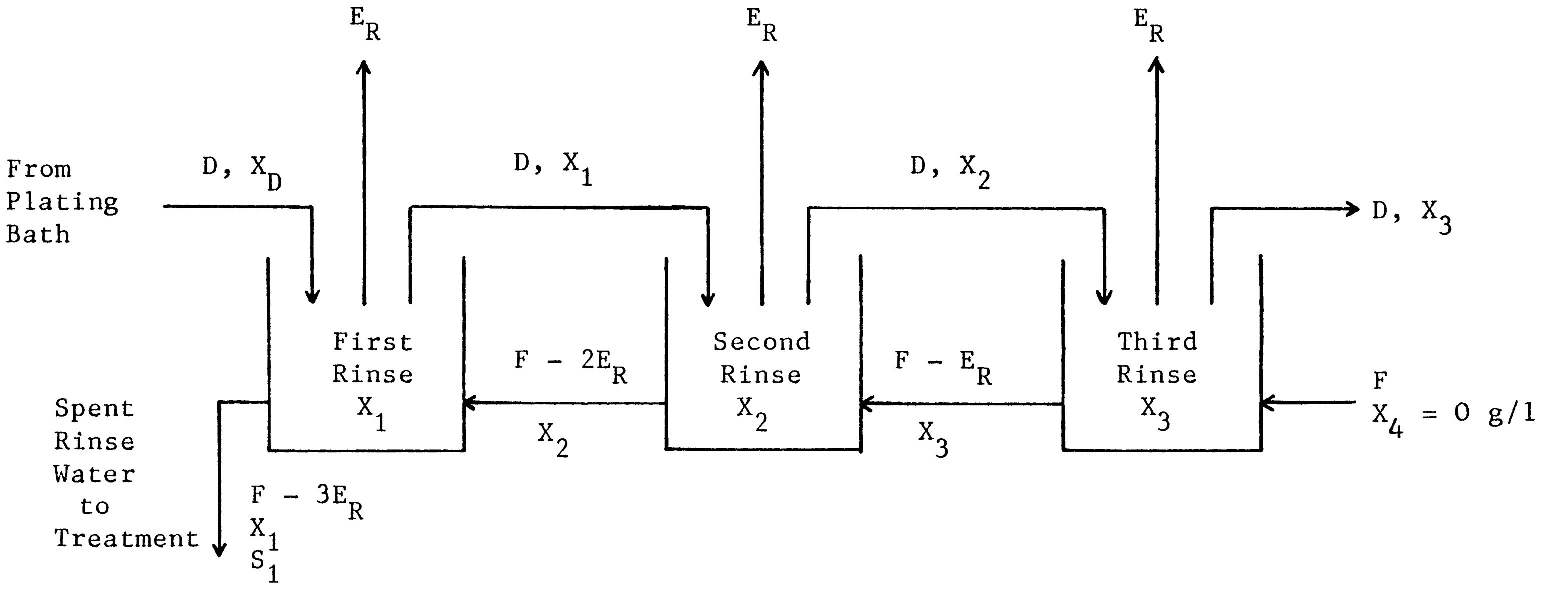

Figure 6. Schematic Diagram of the Existing Rinse System Showing the Variables of Calculation ("X" Denotes Solute Concentration, "S" Denotes Solute Mass Flow Rate, Other Upper Case Letters Denote Total Volumetric Flow Rates).

$= 8.093 \times 10^3$ 1/yr.

Environmental Protection Agency literature provided a graphical estimate for evaporation from rinse tanks as a function of temperature.[19] The lowest temperature at which an estimate was presented was 27 °C. This evaporative flux rate of 0.6424 $1/\text{hr}/\text{m}^2$ was used to approximate evaporation from the rinse tanks as:

$$E_R = (2000 \text{ hr/yr})(0.37 \text{ m}^2)(2 \text{ hrs actual time/hr operative time}) \times (.6424 \text{ 1/hr/m}^2)$$
$$= 9.508 \times 10^2 \text{ 1/hr.}$$

A salt mass balance on the first tank reveals

$$X_1 = \frac{DX_D + (F-2E_R)\,X_2}{D + F - 3E_R}. \qquad \text{(Eq - 1)}$$

From a salt mass balance on the second tank

$$X_1 = \frac{X_2\,(D + F - 2E_R) - (F - E_R)\,X_3}{D} \qquad \text{(Eq - 2)}$$

Equating 1 and 2 and rearranging

$$X_2 = \frac{(F - E_R)(D + F - 3E_R)\,X_3 - D^2\,X_D}{(D + F - 2E_R)(D + F - 3E_R) - D(F - 2E_R)}. \qquad \text{(Eq - 3)}$$

A salt mass balance on the third tank gives

$$X_2 = \frac{X_3(D + F - E_R)}{D}. \qquad \text{(Eq - 4)}$$

Equating 3 and 4 and rearranging produces the following cubic equation in terms of F:

$$F^3X_3 + F^2(D - 6E_R)\,X_3 + F(D^2 + 11E_R{}^2 - 5DE_R)\,X_3$$
$$+ [(D^3 - 6E_R{}^3 - 3D^2E_R + 6DE_R{}^2)\,X_3 - D^3\,X_D] = 0.$$

D, E_R, X_3, and X_D are known. Thus solving for F,

$F = 2.021 \times 10^5$ l/yr.

Solving for X_2 from equation 4 (or 3):

$X_2 = 4.840 \times 10^{-1}$ g/l.

Solving for X_1 from equation 2 (or 1):

$X_1 = 1.199 \times 10^1$ g/l.

The above calculations provide rough targets for flow parameters in the design of the integrated reverse osmosis rinse system. In addition to the assumptions presented earlier, it is assumed that the reverse osmosis unit can reject 98.5% of the solute molecules from passing through its membrane. From the standpoint of first estimate, if 1.5% of the solute in stream F was in the permeate, the amount of solute recycled to the rinse system would be

$$S_P = .015\ S_1 = .015(2.389 \times 10^6 \text{ g/yr})$$

$$= 3.584 \times 10^4 \text{ g/yr.}$$

In order to achieve a steady state concentration of 1.872×10^{-2} g/l in the third tank even when no rinsing is taking place, the permeate concentration would have to be 1.872×10^{-2} g/l. Thus, the minimum permeate flowrate would be

$$P_{min} = \frac{S_P}{X_3} = \frac{3.584 \times 10^4 \text{ g/yr}}{1.872 \times 10^{-2} \text{ g/l}}$$

$$= 1.915 \times 10^6 \text{ l/yr.}$$

This is 9.5 times greater than the rinse water flowrate into the third tank in the existing system.

Performing a similar analysis for recycling the permeate to the second rinse tank

$$P_{min} = \frac{S_P}{X_2} = \frac{3.584 \times 10^4 \text{ g/yr}}{4.84 \times 10^{-1} \text{ g/l}}$$
$$= 7.405 \times 10^4 \text{ l/yr.}$$

This is only 37% of the rinse water flowrate into the second rinse tank in the existing system. Thus, it appears that the existing rinse system could handle the flowrates resulting from recycling the permeate to the second rinse tank. More detailed calculations that include solute added from rinsing the parts, water loss from evaporation, and water and solute added as make-up to the system are needed to confirm this.

A schematic diagram of the proposed system showing the variables used in the following calculations is presented in Figure 7. The dragout flowrate D and its solute concentration out of the plating bath X_D remain the same as in the existing system. Make-up rinse water, designated by flowrate M, comes from the third rinse tank, which is not shown. Its solute concentration remains the same as the third tank in the existing system, 1.872×10^{-2} g/l. If the flow of rinse water through the third bath is to be the same as it is currently, the amount of solute entering it must be the same. Therefore, X_2 equals 4.840×10^{-1} g/l. It is assumed that make-up plating bath fluid, N, has the same solute concentration as the plating bath, or $X_N = 2.952 \times 10^2$ g/l. Evaporation from each rinse tank E_R is the same as in the existing system. It is assumed that the four plating baths are operated 1 hour every 2 hours. When operating the temperature is 54 °C. When off, the temperature is assumed to be 27 °C. The Environmental Protection Agency literature

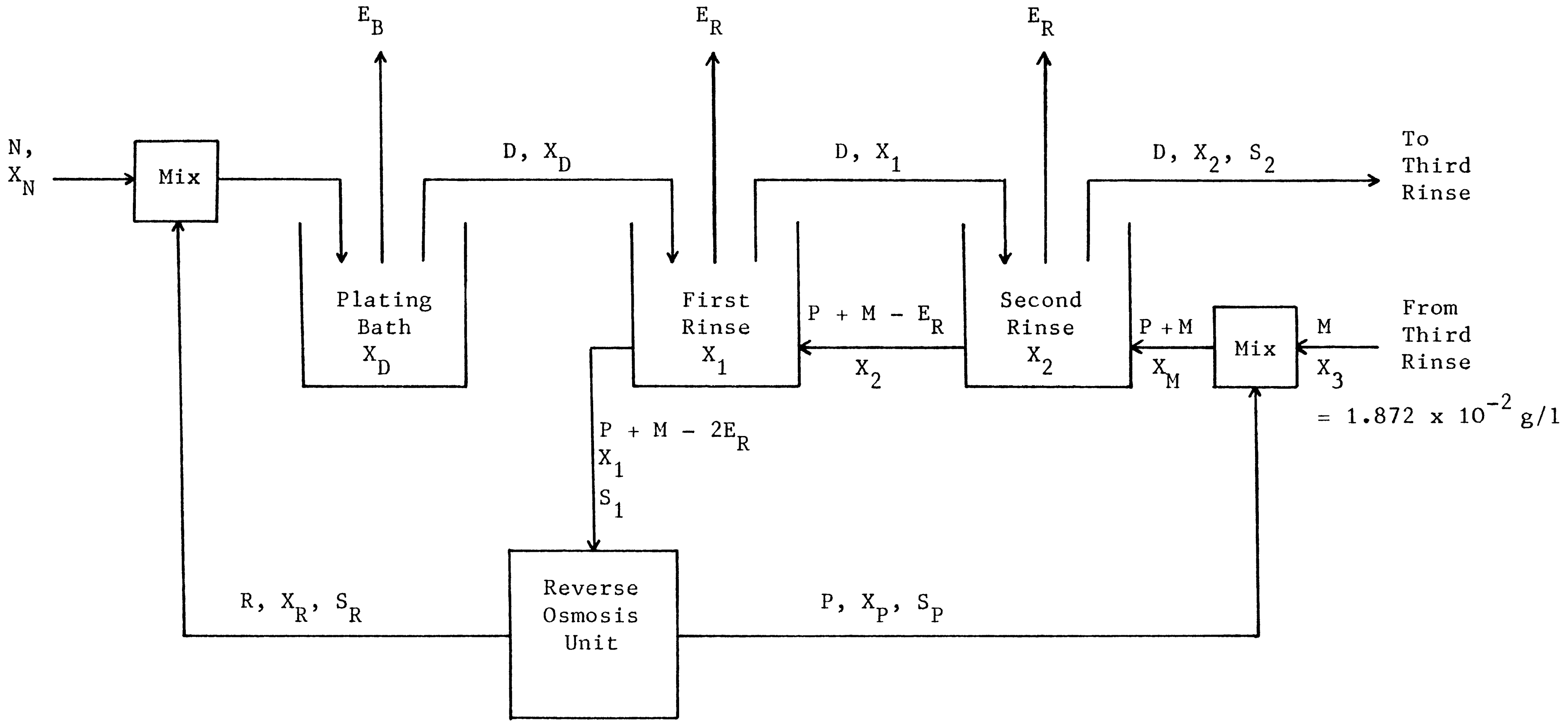

Figure 7. Schematic Diagram of the Proposed Integrated Reverse Osmosis Rinse System Showing the Variables of Calculation ("X" Denotes Solute Concentration, "S" Denotes Solute Mass Flowrate, Other Upper Case Letters Denote Total Volumetric Flowrates).

shows the evaporative flux rate from a plating bath a 54 °C to be 3.417 $1/hr/m^2$. Thus,

$$E_B = (2000)(0.37)(3.417 + 0.6424)$$
$$= 3.004 \times 10^3 \text{ l/yr.}$$

Solute leaves the system only in dragout from the second rinse.

$$S_2 = DX_2 = (8.093 \times 10^3)(4.840 \times 10^{-1})$$
$$= 3.917 \times 10^3 \text{ g/yr.}$$

A solute mass balance on the overall system gives

$$N = \frac{S_2 - MX_3}{X_N} \qquad \text{(Eq - 5)}$$

A total mass balance on the overall ysstem gives

$$M = E_B + 2E_R = D - N \qquad \text{(Eq - 6)}$$

Combining 5 and 6,

$$N = \frac{S_2 - (E_B + 2E_R + D)\ X_3}{X_N - X_3}$$
$$= \frac{3.917 \times 10^3 - (1.300 \times 10^4)(1.872 \times 10^{-2})}{(2.952 \times 10^2 - 1.872 \times 10^{-2})}$$
$$= 1.245 \times 10^1 \text{ l/yr.}$$

Thus,

$$M = 3.004 \times 10^3 + 2(9.508 \times 10^2) + 8.093 \times 10^3 - 1.245 \times 10^1$$
$$= 1.299 \times 10^4 \text{ l/yr.}$$

Considering only the rinse and reclaim system as shown in Figure 8, a total mass balance on the overall system gives

$$R = M - 2E_R$$
$$= 1.299 \times 10^4 - 2(9.508 \times 10^2)$$
$$= 1.109 \times 10^4 \text{ l/yr.}$$

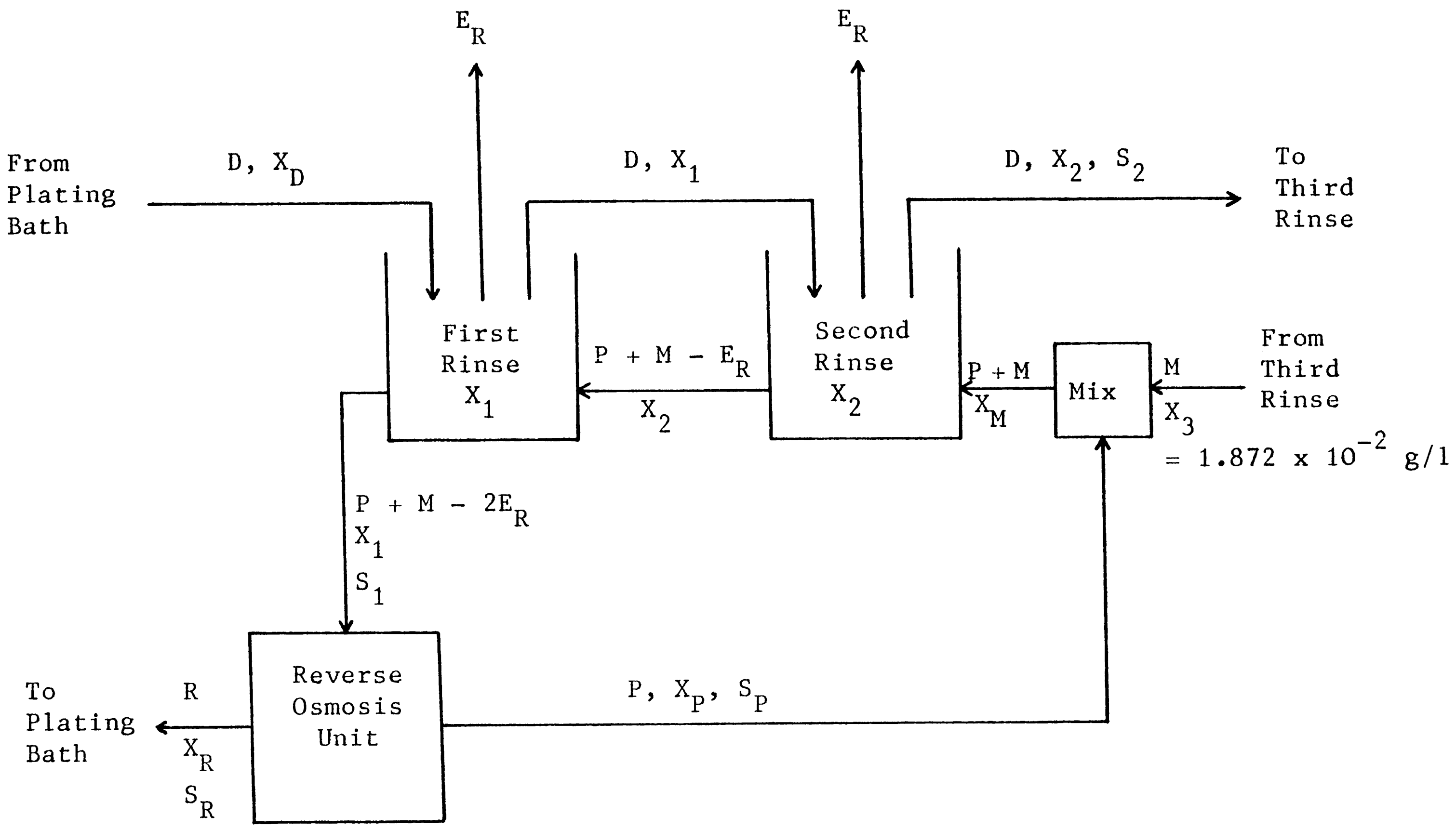

Figure 8. Schematic Diagram of the Rinse and Recovery Section of the Proposed Integrated Reverse Osmosis Rinse System ("X" Denotes Solute Concentration, "S" Denotes Solute Mass Flowrate, Other Upper Case Letters Denote Total Volumetric Flowrates).

A solute mass balance on the rinse and recycle system reveals

$$X_R = \frac{D(X_D - X_2) + MX_3}{R}$$

$$= \frac{(8.093 \times 10^3)(2.952 \times 10^2 - 4.84 \times 10^{-1})}{1.109 \times 10^4}$$

$$+ \frac{(1.299 \times 10^4)(1.872 \times 10^{-2})}{1.109 \times 10^4}$$

$$= 2.151 \times 10^2 \text{ g/l}$$

The total solute in R is

$$S_R = RX_R = (1.109 \times 10^4)(2.151 \times 10^2)$$

$$= 2.386 \times 10^6 \text{ g/yr.}$$

If the solute rejection of the reverse osmosis unit is 98.5%, the total solute into the unit is

$$S_1 = \frac{S_R}{.985} = \frac{2.386 \times 10^6}{.985}$$

$$= 2.422 \times 10^6 \text{ g/yr}$$

and the solute in the permeate stream is

$$S_P = .015\ S_1 = .015\ (2.422 \times 10^6)$$

$$= 3.633 \times 10^4 \text{ g/yr.}$$

A solute mass balance on the first rinse produces

$$X_1 = \frac{DX_D + (P + M - E_R)\ X_2}{D + P + M - 2E_R} \qquad \text{(Eq - 7)}$$

Similarly for the second rinse,

$$X_1 = \frac{(D + P + M)\ X_2 - (P + M)\ X_M}{D} \qquad \text{(Eq - 8)}$$

Equating 7 and 8 and rearranging

$$(D + P + M - E_R)(D + P + M - 2E_R)\ X_2 -$$

$$(P + M)(D + P + M - 2E_R)\ X_M - D^2X_D - D(P + M - E_R)\ X_2$$

$$= 0. \qquad \text{(Eq - 9)}$$

A solute mass balance on the mixer results in

$$X_M = \frac{PX_P + MX_3}{P + M}$$

but

$$P = \frac{S_P}{X_P} \qquad \text{(Eq - 10)}$$

so

$$X_M = X_P \left(\frac{S_P + MX_3}{S_P + MX_P} \right) \qquad \text{(Eq - 11)}$$

Substituting 10 for P and 11 for X_M into 9 and rearranging yields the quadratic equation

$$\begin{aligned} &X_P{}^2 \, (D^2X_2 + DMX_2 - 2DE_R \, X_2 + M^2X_2 - 3ME_R \, X_2 \\ &+ 2E_R{}^2 \, X_2 - DS_P - MS_P + 2E_RS_P - D^2X_D \\ &- DMX_3 - M^2X_3 + 2ME_RX_3) \\ &+ X_P(DS_P \, X_2 + 2MS_P \, X_2 - 3E_RS_PX_2 - S_P{}^2 - MS_PX_M) \\ &+ S_P2 \, X_2 = 0 \qquad \text{(Eq - 12)} \end{aligned}$$

D, M, E_R, X_2, X_3, and S_P are known.

Thus 12 is of the form

$$aX^2 + bX + c = 0$$

where:

$a = - 1.990 \times 10^{10}$ l·g/yr^2;

$b = - 7.797 \times 10^{8}$ g^2/yr^2;

$c = 6.388 \times 10^{8}$ g^3/l·yr^2.

Solving,

$X_P = 1.607 \times 10^{-1}$ g/l.

Solving for P by 10,

$$P = \frac{S_P}{X_P} = \frac{3.633 \times 10^4}{1.607 \times 10^{-1}}$$

$$= 2.261 \times 10^5 \text{ l/yr.}$$

Total flow into the second rinse is

$$P + M = 2.261 \times 10^5 + 1.299 \times 10^4$$

$$= 2.391 \times 10^5 \text{ l/yr.}$$

This is only 19% greater than the existing rinse water flow rate into the second rinse. This increase should present no problem to the existing rinse system.

The flowrate out of the first rinse tank and to the reverse osmosis unit is

$$P + M - 2E_R = 2.391 \times 10^5 - 2(9.508 \times 10^2)$$

$$= 2.372 \times 10^5 \text{ l/yr.}$$

The solute concentration of this feed stream is

$$X_1 = \frac{S_1}{P + M - 2E_R} = \frac{2.422 \times 10^6}{2.372 \times 10^5}$$

$$= 1.021 \times 10^1 \text{ g/l.}$$

The permeate flowrate (P) out of the reverse osmosis unit is 2.261×10^5 l/yr. The remaining flowrate (R) of 1.109×10^4 l/yr leaves the unit as concentrate.

The Environmental Protection Agency[19] cites a permeate flux rate of 12.22 l/hr/m^2 for a reverse osmosis unit operating with a solute feed concentration of 3000 mg/l and a permeate to feed ratio of 0.95. As calculated above, the permeate to feed ratio is 0.953. However, the feed concentration is approximately 10,000 mg/l. The Environmental Protection Agency literature[19] states that doubling the feed concentration to a reverse osmosis reduces the flux rate by 25 percent. Thus, a feed concentration of 6000 mg/l should reduce the flux rate to 9.165 $l/hr/m^2$. Similarly a 12,000 mg/l feed concentration should result in a flux rate of 6.874. A least-squares fit of a quadratic equation to these points produces the following function for the flux rate in terms of feed concentration:

$$Q = (7.073 \times 10^{-2})\ X^2 - (1.655)\ X + (16.55)$$

where:

Q = the permeate flux rate in $l/hr/m^2$

X = the feed concentration in g/l.

Therefore, if the feed concentration is 10 g/l the permeate flux rate should be 7.073 $l/hr/m^2$. Using this, the required reverse osmosis membrane area is

$$A = \frac{(2.261 \times 10^5\ l/yr}{(7.073\ l/hr/m^2)(2000\ hrs/yr)}$$

$$= 1.599 \times 10^1\ m^2$$

Data presented in the Environmental Protection Agency literature[19] suggests that the minimum size reverse osmosis unit available has a membrane area of about 32.5 m^2 and a 1979 cost of approximately $15,000. This is the unit proposed to recycle the nickel plating solute currently being disposed of in stream number 12.

Perry[25] gives the following equation for calculating the hydraulic horsepower of a pump:

$$\text{Hydraulic hp.} = \frac{H_p\ (gal/min)}{1714}$$

where

H_p = total dynamic head in lg/sq.in.

The flowrate in gal/min to the reverse osmosis unit is

$$\text{Gal/Min} = \left(\frac{2.372 \times 10^{5} \text{ l/yr}}{2000 \text{ hr/yr}} \right)\left(\frac{1 \text{ hr}}{60 \text{ min}} \right)\left(\frac{1 \text{ gal}}{3.785 \text{ l}} \right)$$

$$= 5.222 \times 10^{-1}.$$

Assuming a total dynamic head of 800 lb/sq.in., the hydraulic horsepower required to operate the reverse osmosis unit would be:

$$\text{Hydraulic hp.} = \frac{(8.000 \times 10^{2})(5.222 \times 10^{-1})}{(1.714 \times 10^{3})}$$

$$= 2.438 \times 10^{-1} \text{ hp.}$$

A regenerative pump is particularly useful for handling low volumes of low viscosity liquids at high pressures and would be a good choice for this application. Perry[25] presents a performance curve for regenerative pumps. The maximum pump efficiency shown is less than 50%. Therefore, a pump efficiency of 30% is deemed reasonable here. If the electric motor driving the pump is 80% efficient, the required power input to the motor is:

$$\text{Input hp.} = \frac{2.438 \times 10^{-1} \text{ hp}}{(.3)(.8)}$$

$$= 1.016 \text{ hp.}$$

Thus, a one horsepower motor should be sufficient to drive the pump.

APPENDIX C

Calculation of Discounted Cash Flow Rate of Return of Nickel Plating Solute Recycling Using an Integrated Reverse Osmosis Rinse System

The following parameters must be estimated to project the discounted cash flow rate of return for the integrated reverse osmosis rinse system:

(1) fixed capital investment;

(2) working capital investment;

(3) cash flow after plant startup.

In this project, it is assumed that the fixed capital investment, which includes the cost of engineering, equipment, and installation, is disbursed at a constant and continuous rate throughout a design and construction period of 6 months. The working capital is then supplied at time zero (process startup).

Table 20 presents a summary of the estimated total investment required for this project in 1979 dollars. Most of the direct cost items were taken directly from Environmental Protection Agency literature.[19] However, piping and miscellaneous installation costs were increased significantly over those projected by the Environmental Protection Agency. These costs were increased because the generator stated that insufficient space was available for the reverse osmosis unit adjacent to the existing plating line. The unit would have to be located somewhere in the basement of the

TABLE 20

Summary of Estimated Total Investment for Proposed Reverse Osmosis System[19,22] (1979 Cost) - $49,500

I. Fixed Capital Investment	$39,600
A. Direct Cost	$25,000
1. Equipment	$21,000
a. Reverse osmosis unit w/50 μm filter and centrifugal pump	$15,000
b. Activated carbon filter	$ 2,000
c. Piping	$ 2,500
d. Miscellaneous	$ 1,500
2. Installation labor and materials	$ 4,000
a. Site preparation	$ 200
b. Plumbing	$ 2,500
c. Electrical	$ 500
d. Miscellaneous	$ 800
B. Indirect Cost	$11,200
1. Engineering and supervision	$ 7,400
2. Construction expense	$ 2,500
3. Contractors fee	$ 1,300
C. Contingency	$ 3,600
II. Working Capital Investment	$ 9,900

building. Thus, the interconnecting piping system could constitute a considerable portion of the direct costs.

The indirect costs and contingency presented in Table 20 were derived from cost factors presented by Peters and Timmerhaus.[22] This was also the source of the cost factor used to estimate the working capital investment as 20% of the total investment. Thus, in 1979 dollars, the total investment is estimated to be \$49,500 of which \$39,600 is fixed capital and \$9,900 is working capital.

The annual CE plant index for 1979 is 238.7. The CE plant cost index for December, 1982 is 314.3.[21] Scaled to December, 1982 dollars, the total investment for the project is estimated to be

$$49{,}500 \left(\frac{314.3}{238.7} \right) = \$65{,}200.$$

Using the previously presented factor, the estimated working capital is \$13,000 and the estimated fixed capital is \$52,200.

Cash flow from the project after plant startup is actually the result of savings incurred from reduced plating chemical usage and reduced disposal costs. Estimates of the following information are needed to estimate cash flow:

(1) savings incurred from reduced plating chemical and disposal costs;

(2) additional total cost of operation of the integrated reverse osmosis rinse system over that cost for the existing rinse system;

(3) taxes on additional profits generated by using the recycling system;

(4) depreciation of the fixed capital investment.

Prior to process startup, the values of these items are assumed to be zero. After startup, they are assumed to be continuous and constant with respect to time.

The current cost to dispose of stream number 12 in a hazardous waste landfill is estimated to be $60,000 each year. The landfill is located out of state. A regulatory exclusion for the waste would allow the generator to dispose of the waste in an industrial waste landfill. There is a good possibility that an adequate disposal facility could be found closer to the generator thus reducing waste transportation costs. In all, it is assumed here that half of the disposal cost presented above could be saved.

In addition to reducing disposal costs, the recycle system would reduce plating chemical usage and costs. The 1979 costs for plating chemicals were taken from Environmental Protection Agency literature[19] and scaled to approximate 1982 costs by multiplying by 1.3. As shown in Table 21, the savings incurred from reduced chemical usage is minor compared to savings in disposal costs.

The projected cost of operation of the reverse osmosis system is presented in Table 22. Most of the cost items shown were based on information given in the Environmental Protection Agency literature.[19] Labor cost was assumed to be $15/hr. The 1979 membrane cost given by the Environmental Protection Agency was scaled to December, 1982 cost using

TABLE 21

Estimated Annual Savings from Integrated Reverse Osmosis Rinse System - $31,660

Item	Amount	Unit Value	Total Value
$NiSO_4$	4.855×10^2 kg	$1.96/kg	$ 950
$NiCl_2$	2.648×10^2 kg	$2.68/kg	$ 710
Disposal Cost	(one half current disposal costs)		$30,000
		Total Savings	$31,660

TABLE 22

Summary of Estimated Annual Cost of Operation for Proposed Reverse Osmosis System[19,22] (1982 Cost) - $19,110

I.	Annual Operating Costs	$11,020
	A. Labor: 100 hr/yr at $15.00/hr	$ 1,500
	B. Maintenance and operating supplies: 12.65% of fixed capital investment	$ 6,600
	C. Plant overhead	$ 860
	D. Raw materials	$ 1,970
	1. Replacement membranes: 3/yr at $440.00	$ 1,320
	2. Resin for carbon filter	$ 650
	E. Utilities: 2,000 kwh at $0.45/kwh	$ 90
II.	Fixed Costs	$ 8,090
	A. Depreciation: 10% of total investment	$ 6,520
	B. Taxes and insurance	$ 1,570

CE fabricated equipment cost indices. Other 1979 costs were scaled to 1982 cost by multiplying by 1.3. Depreciation was calculated using the straight line method based on a 10 year service life and zero salvage value. Local taxes and insurance were estimated by percentage of fixed capital investment as given by Peters and Timmerhaus.[22]

Assuming a tax rate of 46% on income, cash flow was calculated as follows:

$$I = S - E = \$31.660 - \$19{,}910$$
$$= \$11{,}750$$
$$T = 0.46I = 0.46\ (\$11{,}750)$$
$$= \$5{,}400$$
$$P = I - T + \$11{,}750 - \$5{,}400$$
$$= \$6{,}350$$
$$C = P + D$$
$$= \$6{,}350 = \$6{,}520$$
$$= \$12{,}870$$

where:

I = income;
S = savings;
E = cost of operation;
T = taxes
P = profits;
C = cash flow;
D = depreciation.

Using an engineering and construction period of 6 months, the time zero value of the fixed capital investment is:

$$B = F\ (e^{0.5r}-1)/0.5r$$
$$= \$52,200\ (e^{0.5r}-1)/0.5r$$

where:

B = the compounded fixed capital investment;

F = fixed capital investment;

r = discounted cash flow rate of return.

The working capital is supplied at time zero and is not compounded

$$W = \$13,000$$

The cash position at time zero is

$$CP_{zero} = B + W$$
$$= \$51,200\ (e^{0.5r}-1)/0.5r + \$13,000.$$

The cash flow after startup is assumed continuous and constant. The time zero value of the cash flow compounded over the 10 year service is:

$$CF_{zero} = C\ \left(\frac{e^{10r}-1}{r\ e^{10r}} \right)$$

$$= \$12,870\ (e^{10r}-1)/re^{10r}$$

When the project is completed, the working capital can be recovered. The time zero value of this money is:

$$WC_{zero} = W/e^{10r}$$
$$= \$13,000/e^{10r}$$

To break even the value of the money paid out must equal the value of the money recovered. Thus the rate or return, r, must be found such that:

$$CP_{zero} = CF_{zero} + WC_{zero}$$

The rate of return was found by trial and error to be 15.8%.

The undersigned, appointed by the Dean of the Graduate Faculty, have examined a thesis entitled

Hazardous Metal Wastes: Landfill Alternatives

presented by

Lloyd Gregory Cook

a candidate for the degree of

Master of Science

and hereby certify that in their opinion it is worthy of acceptance.

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