Research and Development

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# **Project Summary**

# An Investigation of Foreign By-Product Coke Plant and Blast Furnace Wastewater Control Technology and Regulation

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This study was to determined more effective wastewater control technologies for by-product coke plant and blast furnace gas cleaning wastewaters are being used in foreign plants than in domestic ones. Some unusual techniques for the treatment of blast furnace gas cleaning wastewaters were found. Aeration of the wastewater prior to clarification improved settling and allowed a greater rate of recirculation. Filtering the wastewater through slag or flue dust removed cyanide.

Treatment of by-product coke plant and blast furnace gas cleaning wastewater is, in general, not more advanced in foreign plants than in the United States. However, blast furnace gas cleaning water in foreign plants is generally recycled to a greater degree. Also, highly qualified and experienced wastewater treatment plant operators and high level plant management involvement were frequently observed at foreign plants. A noticeable spirit of cooperation between regulators and industry was observed in many countries.

Discussions were held with plant and corporate personnel at 26 plants in 14 countries and with regulatory agencies in 10 of the 14 countries to determine the regulations imposed upon the plants, the incentives provided to reduce pollution loads to receiving waters, and to investigate treatment technology.

Recommendations for research projects are made as there appear to be promising areas for improvement of wastewater treatment techniques.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

## Introduction

In its continuing effort to make information available on the most advanced and efficient methods of reducing water pollution from iron and steel production, the U.S. EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, contracted with Hydrotechnic Corporation to perform an engineering study of foreign steel plants. This was to determine if water pollution control practices were being employed for byproduct coke plant and blast furnace wastewaters that were superior to those used in the U.S. In fulfillment of this contract, Hydrotechnic visited 25



plants in 14 countries, excluding the U.S., Canada, and Eastern Bloc nations. The plants visited accounted for over 23 percent of all steel produced outside of the three areas excluded. One of the plants visited was a by-product coke plant only and one plant consisted of a single blast furnace.

Three factors were considered in the selection of the plants to be evaluated:

- Based on a literature search and personal correspondence, the likelihood of the plants utilizing exemplary or innovative treatment technology.
- Based on prior investigation, the relative abundance or lack of process water in the plant area.
- Based on literature, the degree of environmental concern in the countries where the plants are located.

Of the 25 plants visited, 23 provided information that was useable to permit evaluation of their wastewater treatment systems. These 23 plants are listed below by country.

ARGENTINA - Plant requested anonymity

AUSTRALIA - Broken Hill Proprietary - Newcastle Works
- Australia Iron & Steel - Hoskins Kembla Works

BELGIUM - SIDMAR
ENGLAND - British Steel - Scunthorpe

FRANCE - Pont-a-Mousson
ITALY - Italsider
- Taranto Works

JAPAN - Nippon Kokan KK - Ogishima

Works

Works

Orgreave

Works
- Sumitomo Metal
Ind. - Kashima

Works
- Kobe Steel Ltd.
- Kakogawa

Works
- Kawasaki Steel

 Chiba Works
 Altos Hornos de Mexico

Works

NETHERLANDS SOUTH AFRICA

**MEXICO** 

Hoogovens
 ISCOR - Pretoria
 Works
 Newcastle
 Works
 Vanderbiilpark

**SWEDEN** 

- Svenskt StalNorrbottensJarnverk
- Surhammars Bruks -
  - Spannarhyttan

TAIWAN - China Steel WEST GERMANY - Roechling

Burbach

- Thyssen - Hoesch

Huttenwerke

In addition to visiting plants and cooperate engineering staffs, and observing wastewater treatment operations at the production facilities, nine government agencies were consulted. A trade association was consulted in a tenth country. The agencies provided information on how regulations influenced the degrees of treatment and on the incentives provided for increasing recirculation of water within the production facilities.

The nine governments were:

Argentina

Australia (New South Wales)
Japan (two agencies)

Mexico

Netherlands (two agencies)

South Africa Sweden

Taiwan

At the meeting with the trade association, VDEh, an organization of the West German iron and steel industry, several steel company representatives and a representative from the local West German water and waste agency were present.

### Summary

### **By-Product Coke Plants**

The volume of waste ammonia liquor produced at foreign by-product coke plants ranged from 0.14 to 0.24 m³/Mg (34 to 178 gal./ton). These volumes are higher than those found in U.S. by-product coke plants evaluated through the literature.

The treatment of by-product coke plant wastes at foreign plants is basically similar to that practiced in the U.S. Single stage biological treatment is used at 14 of the plants visited. Nine of these 14 add dilution water to reduce high ammonia concentrations in the wastewater to levels not toxic to the organisms. At one plant in Japan, salt water is used. All plants utilizing biological treatment add phosphorus as a nutrient, usually in the form of

phosphoric acid. Two of the plants pretreat the wastes by filtering the wastewater through a coarse coke bed. This procedure removes tar and oil that may be detrimental to the biological oxidation process. Two other plants use tertiary treatment consisting of sand filtration followed by activated carbon adsorption.

Of the 23 by-product coke plants for which some data was available, 14 plants discharged their biologically treated wastewater to public waters, 5 plants treated their wastewater in free ammonia stills and then discharged it 1 plant treated its wastewater in both free and fixed ammonia stills prior to discharge, 1 plant utilized a free ammonia still and a dephenolizer prior to discharge, 1 plant provides no treatment at all prior to discharge, and 1 plant uses the raw waste ammonia liquor together with blast furnace wastewater to irrigate a grass crop that is used for animal feed, reportedly with no ill effects to the animals.

### Blast Furnaces

Blast furnace gas cleaning systems were used at all of the plants visited. The gas washer wastewater application rate varied depending on the type of wet gas cleaning system used. The rates varied from 2.1 to 28 m³/Mg (507 to 6715 gal./ton) of iron produced with an average application rate of 6.09 m³/Mg (1460 gal./ton).

All but one of the plants visited treat their gas washer wastewater for solids removal prior to reuse or discharge. The plant that does not treat is under government directive to provide treatment within the next 2 years. Of the 23 blast furnace installations studied, 3 do not recycle their wastewaters. The remaining 20 plants have recycle rates ranging from 27.4 to 99.2 percent with an average rate of 92.4 percent. Of these plants, 12 had recycle rates equal to or exceeding 98 percent.

Two of the plants treat their blowdowns for cyanide removal. One uses alkaline chlorination and one uses Caro's acid (H₂SO₅). Three other plants reported unexpected cyanide reductions which were not due to planned treatment. One reported that the cyanide reduction is a result of seepage of water through the accumulated sludge in its flue dust ponds, one reported cyanide reduction due to sparging of steam in its clarifier to prevent freezing, and the third reported cyanide reduction when

the gas washer wastewater blowdown was used to quench slag.

### Regulatory Agencies

Regulatory agencies of nine foreign governments were visited to gain insight into the regulatory climate and the relationship that these agencies have with industry. This information provides a better understanding of the individual plant pollution control practices. Countries that are members of the European Economic Community (EEC) have been issued a policy directive with regard to control of water pollution in the EEC. To date, the regulations of the individual countries have taken precedence over the EEC directive.

In addition to the regulatory agencies, VDEh, a West German trade association which represents the iron and steel industry, was visited. Attending the meeting with VDEh were representatives from several steel corporations and a representative of a local West German Federal Government authority.

Only 2 of the 10 countries, Argentina and South Africa, from which regulations were obtained have or will have regulations specific to the iron and steel industry. All others have regulations which pertain to the quality of water discharged to, or the effect of the discharge on, the receiving body. The regulations are based on the use that is made of the receiving body; e.g., potable water, fishing, recreation.

Input from outside of government and industry reportedly had little effect on establishing regulations. Generally, the bases for regulations are: preservation of public health, minimizing environmental effects, aesthetic considerations, and water conservation. The economic impact of the regulations on the individual plant, the industry, and the country is considered.

All agencies reported that the industries or individual companies to be affected by proposed regulations are consulted prior to establishing regulations.

In all the countries, variances to the regulations are subject to negotiation both prior and subsequent to promulgation. They may be based on available technology and/or economic conditions. The final regulations that apply to the individual plants may be referred to differently in each country e.g., in England, they are called "consent conditions," and in South Africa, "relaxed standards."

# Comparison between Foreign and U.S. Treatment

A comparison of foreign and U.S. byproduct coke plants and blast furnace wastewater treatment systems reveals that:

- In general, the treatment applied to these wastewaters in foreign plants is similar to that used in U.S. plants.
- Effluents from foreign plants are not monitored for pollutant content to the same degree that U.S. plants are; i.e., more parameters are monitored in the U.S. than in foreign countries.
- Foreign plants generally recirculate blast furnace gas washer water to greater degrees than do U.S plants.
- Waste treatment plant operators at foreign plants are well trained and qualified. They communicate closely with plant management.

Table 1 shows the comparative compliance with U.S. effluent guidelines limitations as presented in the "Development Document for Proposed Effluent Limitations and Standards for the Iron and Steel Manufacturing Point Source Category" (EPA-440/1-80-024-b, December 1980) for the foreign plants observed and the plants for which detailed data was available in the U.S.

Water use efficiency is indicated by comparing the degrees of EPA compliance to mass limitations. A larger portion of the foreign blast furnace treatment systems that meet the guidelines limitations at Best Available Technology (BAT) levels with respect to concentrations also meet the guidelines limitations with respect to mass discharges for suspended solids and cyanide. This indicates that less water is being discharged per unit of production resulting in the lower mass discharges.

## **Innovative Technology**

### **Blast Furnaces**

A unit operation, not known to be practiced in the U.S., was observed at two foreign plants, August Thyssen in West Germany and Chiba Works of the Kawasaki Steel Corporation. It is the aeration of gas washer water prior to settling in clarifiers or thickeners. A portion of the settled sludge is recirculated to the aeration basin to act as a seed for precipitation of carbonates. This operation increases the cycles of concentration while not increasing the

likelihood of scale formation in the recirculation system.

Four methods of cyanide removal, other than alkaline chlorination, from gas washer wastewater were noted. Three of these methods were not utilized as intentional unit operations, i.e., the operation was not for the specific purpose of cyanide removal, although removal was noted. These operations are:

- Sparging steam through the waste. At one plant in Sweden (Spannarhyttan) cyanide reduction was noted after steam sparging. Steam was utilized to prevent freezing of water in the clarifier and apparently resulted in cyanide reduction from an influent concentration of 30 mg/l down to 2.4 mg/l.
- Filtration of blast furnace wastewater through flue dust. Two plants owned by Hoesch-Estel in West Germany utilize sludge disposal as a means of blast furnace gas washer water blowdown. The sludge is discharged to flue dust ponds and the excess water that seeps through is collected in an underdrain pipe and discharges to a river. Alkalinity is added at both plants: at one, in the form of cold mill sludge; and at the other, in the form of caustic (sodium hydroxide). The cyanide concentration in the liquid phase of the sludge was 0.2 mg/l, and the cyanide concentration of the underdrain flow was 0.1 mg/I. The plant has theorized that the reduction is due to metallocyanide complexes being formed and adsorbed on the flue dust. No work has been done to confirm this hypothesis.
- Use of gas washer wastewater for slag quenching. One plant, ISCORslag guenching. One plant, ISCOR's Pretoria Works in South Africa, reported that, when a portion of the gas washer wastewater blowdown is used for slag quenching, the leachate from the slag pile is free of cyanide. The plant has not reported the cyanide content of the raw water but stated that they believe that the lack of cyanide in the leachate is due to biological activity in the slag pile. No work has been done by the plant to verify this hypothesis. The authors disagree with this theory; they feel that biological organisms would not likely be found in recirculating gas washer water or in molten slag. The

**Table 1**. Comparative Compliance of Foreign and U.S. By-Product Coke Plant and Blast Furnace Wastewater Treatment Facilities with U.S. EPA Draft Effluent Guidelines for BPT and BAT

Area	Coke Plant or Blast Furnace	Level of Treatment	Susp. Solids	Total Cyanide	Oil & Grease	Phenolics	Ammonia
Foreign	Coke Plant	BPT	5	7	3	О	9
U.S.	,,	"	100% 100% 6	100% 100% 6	67% 67% 5	3	13% 22% 6
Foreign	,,	BAT	83% 67% 5	100% 83% 7	60% 80% 3	33% 33% 0	50% 50% 9
U.S.	,,	<i>"</i>	40% 80% 6	100% 86% 6	67% 67% 5	3	0 11% 6
Foreign	Blast Furn.	BPT	17% 17% 12	67% 17% 12	60% 80% 0	0 0	33% 17% 4
U.S.	,,	,,	83% 67% 6	100% 100% 6		6	100% 75% 5
Foreign	,,	BAT	83% 50% 12	83% 33% 12		100% 83% 0	80% 80% 4
U.S.	,,	.,	8% 25% 6	42% 42% 6			0 0
0.0.			17% 0	50% 17%		67% 50%	20% 0

NOTE: The data presented in this table are based on information from a limited number of plants.

The U.S. plants are only those for which data were available from the U.S. EPA Development Documents.

The data for foreign plants are for those that were visited during the course of the study and constituted plants thought to have superior technology.

No. of plants for which data is available

% that meet	% that meet				
concentration limit	mass limit				

gas washer water is subjected to temperatures too high to allow biological growth in the recirculating system.

 Pont-a-Mousson in France uses Caro's acid (H<sub>2</sub>SO<sub>5</sub>) for cyanide destruction. The plant discharges a quantity of gas washer water from the flue dust settling pond, on a batch basis, to chemical treatment tanks where the acid is added. It reacts with and oxidizes the cyanide. In the process, some phenol, reduction is also observed.

### Coke Plants

Of the 23 by-product coke plants observed, 14 utilize biological methods to treat their wastewater. At China Steel in Taiwan and at Kawasaki Steel Corporation's Chiba Works, wastes are pretreated by filtration through a bed of coke to remove excess tars that might interfere with the biological process. At China Steel, after the filtration step, sanitary wastes from the entire plant

are combined with the coke plant wastes and treated in an activated sludge process.

One plant combines untreated coke plant wastewater with blast furnace gas washer water blowdown and uses the combined wastes to irrigate grass fields. The grass crop is used for cattle fodder. No ill effects to the cattle have been reported. This method cannot be considered as innovative treatment but rather as a means of disposal, novel to the steel industry.

### Other Observations

John Lysaght (Aust.) Ltd. of Australia was visited to discuss the hot and cold mill water systems at its Westernport Bay Facility. The hot strip mill operates with the lowest blowdown of any such facility in the world and features four recirculating water systems. One is a completely closed non-contact cooling water system for reheat furnace skid cooling. The water of the other three systems is cascaded with the makeup

water consisting of a mixture of a purchased supply and collected storm water. The makeup is applied to the area where highest quality water is required. Blowdown is cascaded from high water quality systems to facilities which may tolerate lower quality. The contact cooling water is filtered, cooled, and recirculated. Blowdown from the system discharges to Westernport Bay via the plant's cold mill effluent lagoon. The plant reports that the total discharge from the mill of 0.2 m<sup>3</sup>/Mg (48 gal./ton) with mass discharges of 0.002 kg/Mg (lb/1000 lb) each of suspended solids and oil.

The cold mill complex (consisting of a hydrochloric acid pickler, a five-stand cold reduction mill, a coating line, and a paint line) is also an excellent example of conservation and reuse which also results in significant pollution control. The key to minimizing plant water use is the segregation of water systems. All non-contact cooling water is collected, cooled, and reused in a separate

system. Sanitary sewage is collected and treated separately. Waste pickle liquor is regenerated in a hydrochloric acid regeneration plant.

The process water is treated in two separate systems. One is the industrial water treatment system in which the relatively clean wastewater from stands 1 and 5 of the cold mill and the pickler process water are treated, cooled. combined with tertiary treated sanitary wastes, and returned to the mill for reuse. The second wastewater treatment system receives the cold mill rolling solution blowdown and dumps, the pickle liquor regeneration plant excess rinse water, galvanizer alkali dumps, and the industrial water treatment plant blowdown. These wastes are treated for discharge to receiving

Plant and corporate managements are intimately familiar with wastewater treatment practiced at the individual plants and are usually apprised of potential problems before they actually occur. Operators, in many cases, are familiar with the theoretical as well as the practical aspects of the treatment plant operations. Therefore, even though the technologies observed are not considered to be more advanced, they do produce, according to the data provided, higher quality effluents.

Generally, housekeeping was observed to be of a high order. Water was not running where it was not needed. In plants where space permitted, green areas were set aside both to enhance the appearance of the physical plant and to reduce noise in the plant environs.

In one blast furnace cast house, all runners were covered with hoods and a vacuum applied. This resulted in a noticeable lack of fugitive emissions.

### **Conclusions**

Based on observation at 25 foreign plants visited that operate by-product coke plants, blast furnaces, or both, it is concluded that the wastewater treatment practiced in foreign plants is basically similar to that practiced in the U.S. Generally, blast furnace gas washer water is recirculated to a greater degree than at U.S. plants.

Two plants in Japan reported that the by-product coke plant wastewater passed through a tertiary treatment phase; i.e., sand filtration followed by activated carbon adsorption. Of all the plants observed or reported, these were the only plants that apparently addressed the problem of priority pollutants;

however, no data with regard to the efficiency of removal of priority pollutants or effluent levels was provided when requested.

Foreign requirements with respect to effluent quality are usually negotiated between government and industry for each plant on a case by case basis. The economic impacts of the requirements are a major concern.

### Recommendations

Research should be conducted to quantify the pollutant reductions attainable and to ascertain the mechanisms by which the reduction of cyanide occurred for two of the methods observed:

- Sparging of steam through wastewater. Research on this method should also include effects on air quality and energy requirements.
- Filtering the wastewater through flue dust. The research on this method should also include possible effects on air quality at sinter plants or briquetting plants if the flue dust containing cyanide is used as a feed stock.

Research should also be conducted to determine the effect of increased recirculation at blast furnace gas washer operations. Specifically, the method of

increasing recirculation by aerating the solids laden gas washer water prior to settling should be investigated.

Treatment of by-product coke plant wastes by biological means is a generally accepted and proven procedure. However, the authors believe that coke plant wastewater can be combined with blast furnace gas cleaning blowdown water prior to treatment. This treatment concept was raised during discussions with steel plant personnel in the U.S. in the past and abroad during this study. The only objection was that heavy metals present in blast furnace wastewater might be toxic to the biological systems. However, lime precipitation should precipitate the heavy metals that are regulated to permissible discharge levels and, in addition, are not toxic to a biological system. If this unit operation is provided, and the pretreated blast furnace wastewaters are combined with by-product coke plant wastes for biological treatment, then chlorination for removal of other oxidizable parameters would not be necessary. Dechlorination would also not be required.

This concept should be confirmed by a well conceived research program. Further research should also be undertaken to verify a second stage biological process to nitrify ammonia in the combined wastewater streams.

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John S. Ruppersberger is the EPA Project Officer (see below).
The complete report, entitled "An Investigation of Foreign By-Product Coke Plant and Blast Furnace Wastewater Control Technology and Regulation," (Order No. PB 82-221 771; Cost: \$18.00, subject to change) will be available only from:

National Technical Information Service 5285 Port Royal Road Springfield, VA 22161 Telephone: 703-487-4650 The EPA Project Officer can be contacted at: Industrial Environmental Research Labora

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