

The disposal of polluted effluents from Mining, Metallurgical and Metal Finishing Industries, their effects on receiving water and remedial measures†

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SYNOPSIS

The adverse effect of acidic mine drainage derived from gold and coal mining operations on the quality of receiving waters is described, together with measures to be taken to counteract this pollution.

The mineral load and the toxic effects from metallurgical and metal finishing industries are also considered.

Attention is drawn to water conservation aspects.

INTRODUCTION

Acidic mine drainage from working and abandoned gold, coal and other mines constitutes a most serious pollution problem. Effluents pumped out from stoped-out underground areas and run-off from mine dumps, owing to their high content of dissolved solids, suspended solids and iron, their low pH value and their possible toxicity, can render the water in the receiving water bodies unfit for many applications, unless costly treatment is applied. Their influence on the quality of surface waters is felt by many industries, involving higher costs for water treatment to meet the quality demand for their boiler and process waters.

Metallurgical processes create severe pollution problems by the discharge of oily and phenolic wastes, or of toxic constituents, e.g. fluorides from the reduction of aluminium ore.

Metal finishing operations are responsible for the disposal of toxic heavy metals and cyanides.

This paper attempts to highlight some of the problems and to show possible avenues for their solution.

WATER QUALITY STANDARDS

The refinement of raw water into drinking water, boiler feed-water or process water for industry costs money. The discharge of polluted effluents may render large bodies of water unfit for subsequent use, unless costly treatment is applied. Whereas organic and bacteriological pollution can generally be effectively removed at economic rates, this is not the case with inorganic pollution. For use in households and industry, however, the limiting factor is the content of mineral dissolved solids in the water.

It is the aim of the Water Act of 1956 to protect our limited water resources from pollution. In terms of Section 21 of the Water Act No. 54, specifications have been promulgated to which any effluent resulting from the use of water for industrial purposes shall conform (see Table I).

In addition, waste water shall not contain any constituents in concentrations which are poisonous to humans, animals, fish or other aquatic life or deleterious to agricultural use.

Whereas the General Standards do not specify a maximum limit for iron, other countries do. In Western Germany, for instance, regional authorities like the Ruhrverband permit a maximum concentration of 2mg/l Fe in industrial effluents, while under the current Pennsylvania Clean Stream Law the discharge of acidic mine drainage waters into streams is limited to an iron content of below 7 mg/l.

TABLE I
WATER ACT NO. 54, 1956, GENERAL STANDARDS¹
Maximum permissible concentrations (mg/l, except where otherwise stated)

pH (value)	5.5-9.5
Colour, odour, taste	absent
Dissolved Oxygen	min. 75% saturation
Faecal coli	nil
Temperature	max 35°C
Chem. Oxygen Demand (COD)	75
Oxygen Absorbed (OA)	10
Total Dissolved Solids (TDS)	not exceeding 500 above intake
Suspended Solids (SS)	25
Sodium (as Na)	not more than 50 above intake
Soap, oil, grease	2.5
Residual chlorine (as Cl)	0.1
Free and saline ammonia (as N)	10.0
Arsenic (as As)	0.5
Boron (as B)	1.0
Hexavalent chromium (as Cr)	0.05
Total chromium (as Cr)	0.5
Copper (as Cu)	1.0
Phenols	0.1
Lead (as Pb)	1.0
Cyanides (as CN)	0.5
Sulphides (as S)	1.0
Fluoride (as F)	1.0
Zinc (as Zn)	5.0

The maximum permissible concentrations of certain constituents in drinking water is shown in Table II.

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TABLE II

THRESHOLD LIMITS FOR DRINKING WATER SUPPLY
(in mg/l, except pH)

	South African Bureau of Standards ²	
	Max. desirable	Max. permissible
pH	6.0-9.0	5.5-9.0
Total Solids	500	2 000
Hardness (as CaCO ₃)	20-200	1 000
Cyanides (as CN)	0.01	0.2
Chloride (as Cl)	250	600
Chromium hexavalent (as Cr)	0.05	0.05
Fluoride (as F)	1.0	1.5
Copper (as Cu)	1.0	1.5
Iron (as Fe)	0.3	0.7
Manganese (as Mn)	0.1	0.4
Magnesium (as Mg)	100	150
Zinc (as Zn)	5	15
Phenols	0.001	0.002
Sulphates (as SO ₄)	250	400

SOURCES OF POLLUTION

Mining Industry

Mining plays an important role in the Republic's economy, contributing about 12½ per cent of the total gross domestic product and about 59 per cent of the value of total exports.³ Compared with this, mining as a whole uses little water, only about 4.2 per cent of the total water utilised as shown in Table III.

TABLE III

COMPARISON OF THE USAGE OF WATER BY THE MINING INDUSTRY IN RELATION TO THE TOTAL USAGE IN THE REPUBLIC OF SOUTH AFRICA, 1960⁴

(in morgen feet/year)

	Surface water	Ground water	Surface and ground	%
Total Mining	3 178 700	426 000	3 604 700	100
	54 200	97 000	151 200	4.2

1 morgen foot = 575 000 gallons = 2 600 m³

Although the mines only use 4.2 per cent of the total amount of water used in the Republic as a whole, the pollution loads carried in mine effluents can impose limitations on the usefulness of the fresh water resources. A typical example is the interaction between the acidic mine drainage from the gold fields of the Witwatersrand and the deteriorating quality of the water in the Vaal-Barrage system.

Table IV shows the good quality of the water ex Vaal Dam, the quality of the polluted tributaries flowing into the Barrage, and the resultant deterioration at the Vaal/Barrage discharge point for 1969 (see Fig. 1).

In a survey into the mineral loads contributed by the Suikerbosch and Klip Rivers into the Vaal Barrage during 1967/68,⁶ carried out by the Chamber of Mines, it has been estimated that of the total mineral load of 644 ton/day total dissolved solids (TDS) discharged via these two tributaries, an average of 440 ton/day originated from pumped-out underground mine water. These estimates were based on an average flow of 22 m gal/day. (In 1957 when most mines were still active this flow of pumped-out mine waters averaged 37 m gal/day.)

TABLE IV

RESULTS OF PHYSICAL AND CHEMICAL ANALYSES OF WATER SAMPLES IN THE WITWATERSRAND CATCHMENT AREA IN 1969⁵

(Monthly average figures)

	Flow, m ³ /sec.		Conductivity*		Total hardness as mg/l CaCO ₃		Sulphates mg/l	
Engelbrecht's Drift Weir	5.7	49.6	165	195	62	74	5	15
Zuikerbosch Weir	0.06	3.1	350	2550	84	868	56	618
Klip River Weir	1.1	6.5	950	1430	366	716	210	628
Taaiboschspruit Weir	0.003	0.16	560	1520	143	276	83	218
Rietspruit Weir	0.031	2.28	400	2020	80	676	79	729
Vaal Barrage Discharge	4.90	42.4	235	825	92	294	28	215
Vereeniging Pump Station	3.7	7.0	203	721	78	274	22	225

*Conductivity in micromhos; to obtain approximate total dissolved inorganic solids, divide by a factor of 1.5.

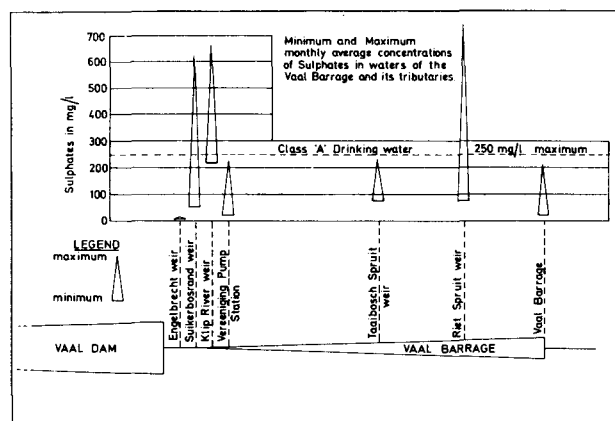


Fig. 1—Sulphate concentration of Vaal Barrage and its tributaries.

The total dissolved solids concentration in the Vaal Dam is more or less constant and is of the order of 100 mg/l. Over a period of almost five years from 1965 to 1969 the monthly maximum for TDS of water abstracted from the Vereeniging pumping station exceeded 500 mg/l during 24 months out of 57 and 700 mg/l during 17 months.

As a result of the progressive decrease in mining activities in the Witwatersrand area it can be expected that there will be a substantial reduction in the total mineral loads discharged from the mines in future. In addition, the covering of the mine dumps by vegetation will materially assist in minimizing the mineral loads derived from this source.

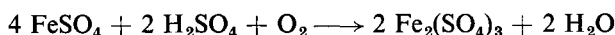
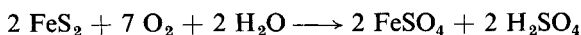
In the Orange Free State, the mines have taken a most commendable action to protect the Vaal River and underground aquifers by using natural pans and by establishing extensive shallow lakes for separate disposal and storage of saline underground water, and by exploiting some of these lakes for recreational purposes.

Remedial measures to combat effects of mine drainage

When considering possible remedial measures to combat the effects of acidic mine drainage, it is important that the causative factors giving rise to the pollution are clearly understood.

Acidic mine drainage is produced as a result of the oxidation of pyrite (FeS_2) and occasionally other metal sulphides present in gold and coal bearing strata. When exposed to air and in contact with moisture, these sulphides react to yield sulphuric acid (H_2SO_4) and ferrous sulphate (FeSO_4); ferrous sulphate is further oxidised to the trivalent ferric sulphate which then hydrolyses to form more acid and insoluble ferric hydroxide.

The following simplified equations may illustrate the mechanism of pyrite oxidation:



In nature these reactions are not as simple as they appear on paper. Bacterial action, for instance, catalytically accelerates the oxidation of pyrite at a tremendous rate, compared with a sterile sample under identical conditions, as has been proved by Van Zyl.⁷

The results of his laboratory-scale oxidation experiments on pyrite in the presence of bacteria and under sterile conditions are shown in Table V.

TABLE V
OXIDATION OF PYRITE SUSPENSION IN WATER⁷

Oxidation time hours	mg Fe dissolved	
	With bacteria	Sterile sample
0	0	0
264	252	4
366	595	not determined
556	1 130	not determined
720	1 445	15

At least four different types of bacteria have been isolated which accelerate the oxidation of pyrites; *Ferrobacillus ferro-oxidans*, *Ferrobacillus sulfo-oxidans*, *Thiobacillus thio-oxidans*, and *Thiobacillus ferro-oxidans*.

Further research should be conducted on methods to inhibit the activity of acid-producing bacteria; if successful, the results would be of great importance to the mining industry.

The reaction speed between pyrite, air and moisture is apparently also influenced by cleavage planes in crystalline structure and the degree of pulverisation.

The composition of untreated acidic drainage from underground mines is shown in Table VI.

The pH of acidic mine water is seldom lower than 2.0, the reason being that ferrous sulphate acts as a buffer between pH 2.0 to 4.0. Acidity, expressed as CaCO_3 , of mine effluent ranges from 100 to 12 400 mg/l. Acidic mine water is highly corrosive; steel pipes, pumps, cables, rails, concrete structures are corroded at a fast rate. Introduction of plastic pipes has been a great improvement. Neutralisation with lime, the cheapest neutralising agent, creates new problems such as crystallisation of calcium sulphate and consequent blockage of pipes.

TABLE VI

CHEMICAL COMPOSITION OF WASTE FLOWS DISCHARGED FROM UNDERGROUND GOLD AND COAL MINES

(in mg/l, except pH)

	Gold mines	Coal mines
pH	3-5	2.8-6.2
TDS	1 100-5 000	800-9 000
Fe	200-600	150-720
SO_4	630-2 500	660-6 700
F*	0-5	0-15

*The occurrence of fluorides in mine effluents is not general and is confined to only a few mines.

Unfortunately, the production of acidic mine drainage does not cease when mining is discontinued. It is known that, in some mines in Natal, water may continue to drain from abandoned workings for years and still contain 4 000-5 000 mg/l TDS, mainly ferrous sulphate. Outcropping coal seams usually remain a permanent source of pollution.⁸

From the foregoing it is clear that the whole problem of pollution by mine effluents has built up progressively as mining activities expand over the years and requires the concerted efforts of the mines, local and regional authorities and government bodies in order to find practicable solutions.

According to Section 21 of the Water Act, any effluent discharged into a public stream must conform to the limits set by the General Standards (Table I). This means that acid mine effluents have to be neutralised.

Adjusting the pH of acid mine drainage with lime is an old technique. For liming, three types of lime can be used, unslaked lime (CaO) with 80-90 per cent calcium (as CaO), hydrated lime (Ca(OH)_2) with 60-70 per cent calcium (as CaO), and dolomitic lime ($\text{CaCO}_3 + \text{MgCO}_3$) with 50 per cent calcium (as CaO).

The use of solid lime is not recommended since an impermeable coating of CaSO_4 is formed which reduces the efficiency of utilisation. Mixing with water is, therefore, essential.

Some mines mix unslaked lime with water in an above-ground installation and pipe the lime slurry into the underground workings for neutralising the acid mine water; other mines with smaller acid flows prefer the use of hydrated lime for convenience, as it can be carried in bags for use underground, whereas some coal mines even use dolomitic lime. The choice of neutralising agent is governed by the factors of economics, railage costs, convenience and safety of handling. One disadvantage of using limestone (CaCO_3) is the long reaction period needed to treat acid drainage high in ferrous iron, while with hydrated lime Ca(OH)_2 the same water is more rapidly neutralised although the sludge produced occupies a larger volume. When lime and limestone are used together a synergistic effect takes place. The time to oxidise ferrous sulphate is reduced and both sludge settling rate and sludge density are improved.

Another technique in treating acidic mine effluents with extremely high ferrous sulphate content, where neutralisation alone will not be adequate to precipitate the iron as stable ferric hydroxide, is to provide additional aeration following the neutralisation (see Fig. 2). This practice is applied at coal mines in the United States of America.⁹

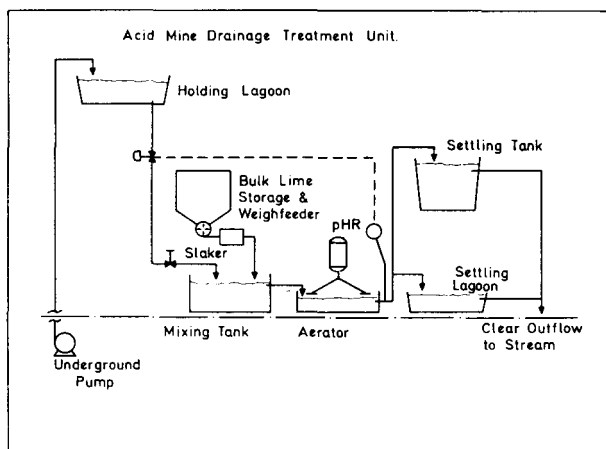


Fig. 2—Neutralisation of acid mine drainage with additional aeration for complete precipitation of iron.

For every ton of lime used about $2\frac{1}{2}$ tons of gypsum (CaSO_4) are produced. As calcium sulphate is partly soluble in water (about 2 000 mg/l), the calcium hardness in the receiving water, e.g. Vaal Barrage, is increased.

Neutralised mine drainage containing CaSO_4 in solution (up to 2 000 to 4 000 mg/l) appears to have a beneficial effect on irrigation in that it counteracts the adverse conditions caused by soda-alkalinity.

Other processes investigated in the U.S.A. include flash-evaporation, electrochemical treatment and ion-exchange. Westinghouse is to build a 5 mil gal/day flash-evaporation plant to convert acidic mine drainage to ultra-pure water (1-10 mg/l TDS); the State of Pennsylvania hopes to pay off the operating costs by selling the high-purity water to industry.

The costs for the electro-chemical treatment project still in the planning stage are to be covered by selling the by-product hydrogen. Ferrous iron will be oxidised to the ferric state and precipitated in settling ponds.

The first large-scale demonstration plant for ion-exchange treatment of acidic mine drainage is to be constructed at Philipsburg, Pa., based on the DESAL-process by Rohm and Haas. The plant will have a capacity of 0.5 million gal/day, and will later be expanded to 1 million gal/day. In reducing the TDS by 1 000 mg/l, unit costs are estimated at \$1 per 1 000 gallons. The recovered water will be of potable quality.¹⁰ This cost is equal or more than that of distillation techniques which have already been considered as an uneconomical means of reducing the mineral load in mine drainage.

The most effective way, however, to reduce the magnitude of acidic mine drainage is *prevention*. Since the oxidation of pyrite is a function of time, and availability of air and water, any approach to reduce pollution requires the control of one of these factors. On active mines, prevention of ingress of water into the workings is the obvious answer. This can be achieved by grading the surface area around the mines to ensure good run-off, or by provision of a sufficient number of adequately sized concrete-lined channels to collect and to divert storm-water.

On mine dumps the leaching out of acidic effluents with their surge flows and loads after rainstorms is prevented by the planting of vegetation.

In establishing vegetation on mine dumps, many obstacles have to be overcome. Problems encountered are: deficiency in plant nutrients, fine sand that destroys

plant life when wind-blown, acidity which affects germination of plants, and lack of essential microbial population. The sloping sides of waste dumps receive greatly varying amounts of solar radiation; therefore, vegetation suitable for northern and western exposures may not be suitable for southern and eastern slopes. The Chamber of Mines has been investigating all these aspects for years and has found ways to overcome these obstacles. At present, new vegetation is being established on mine dumps at a rate of about 1 000 acre/year.

Other measures to prevent run-off and mineral pollution from slimes dams are:

- (i) Provision of trenches around the slimes dams to divert storm-water run-off into designed evaporation areas.
- (ii) Returning water from the top of the slimes dams after prior settling.¹¹

In a most commendable effort to co-ordinate existing knowledge and to instigate positive action by the mines themselves, the Chamber of Mines has formulated codes of practice applicable to coal and gold mines for the effective control of acidic mine drainage. The progressive implementation of these codes will undoubtedly result in a marked improvement in the mineral quality of mine drainage and will reduce these problems to manageable proportions.

Mineralised mine and industrial effluents could be harnessed by the establishment of salt water lakes or dams.^{12, 13} There are many uses to which mineralised water could be put such as cooling water and various process waters for selected industries requiring low quality water. Such lakes and dams can also be exploited to great benefit for recreation which could make a major contribution to the mental health and physical well-being of the people living in the densely populated area of the Witwatersrand. Salt water environments are already exploited in this manner in the Orange Free State, as mentioned previously, as well as on the Witwatersrand.

Such localised impoundment of large volumes of mineralised water may favour large-scale desalination should these processes become economically feasible.

Suitable dam sites for the purpose of creating salt water environments already exist on the Witwatersrand, the Far West Rand and the Orange Free State goldfields area. We can expect that the implementation of the aforementioned codes of practice by the mines will cut down the quantities of effluents to manageable proportions.

The whole problem and the implementation of such large-scale projects, however, are of such magnitude that the mines alone cannot handle it and, therefore, the co-operation and assistance of the Government, local and regional authorities is essential. It may well be that the contribution which salt water environments may make to the conservation of the water household of the area as a whole will justify the planning of these schemes on a national level on the same basis as that for fresh water supply dams.

Metallurgical Industry

Effluents from steelworks contain phenols, cyanides, ammonia, tar and tar oils, produced by the coke ovens and by-products section; flue dust and sludge originate from the blast furnaces, from the basic oxygen and open hearth furnaces; mill scale, sludge and oil are derived from hot rolling and cold reduction mills.

Fluorides in waste waters originate from the L/D (Linz/Donawitz) steel-making process, from the reduction of bauxite to aluminium or from electrolytic tinning.

Furnace gas washers contain particles of submicron sizes which are extremely difficult to separate by sedimentation; cyanides are a problem specific to the production of ferro-manganese.

Cleaning operations in metal finishing produce waste waters containing emulsified oils, alkali and solvent residues; the largest waste volume from cleaning is spent pickle liquor, usually spent H₂SO₄ containing FeSO₄. Spent pickle solutions represent the most difficult waste water problem of the metal finishing industry on account of their high acidity and high concentration of dissolved metal.

The various plating operations, particularly electrolytic tin-plating, galvanising and chromium-plating produce waste waters containing toxic metals in solution, as well as toxic cyanides.

The general trend in the steel industry is to produce products of lighter unit weight. Wastes, however, are generated in proportion to the surface area of steel exposed during rolling and finishing operations. Therefore, with lighter unit weights greater unit waste loads are produced. Electrolytic tin-plating and galvanising

tend to replace hot-dip processes due to the higher production rates possible and due to the reduced amount of plating metal in the wet processes. Consequently, metal-containing effluents are produced nowadays which were not previously generated with hot-dipping processes.

Where industrial effluents are discharged directly into public streams, their quality after purification must comply with the specification of the General Standards. Most of our secondary industries are, however, situated within municipal boundaries and discharge their effluents into municipal sewers. In this case the municipalities with their treatment facilities accept the responsibility of discharging a purified effluent which complies with the General Standards. Municipalities with their large proportion of domestic and other biodegradable effluents are capable of handling more concentrated trade wastes, therefore municipal drainage by-law regulations are, in many respects, more lenient than the General Standards as shown in Table VII.

In waste flows from steelworks and metal finishing plants objectionable components are found in concentrations by far in excess of the permissible limits of the General Standards or of the more lenient municipal drainage by-laws. Spent pickle liquors contain free and dissolved metals, usually iron or zinc, in concentrations of up to 100 g/l, and have a pH around 1.

TABLE VII
MAXIMUM PERMISSIBLE CONCENTRATIONS FOR INDUSTRIAL
EFFLUENTS DISCHARGED INTO MUNICIPAL SEWERS

(All units in mg/l, except otherwise stated)

	Johannesburg	Pretoria	East London	Germiston*
pH	> 6.0	6-10	6-10	6.5-12
Chemical Oxygen Demand (COD)	N.S.	5 000	N.S.	N.S.
4 hrs. OA	1 400	200	N.S.	N.S.
Temperature	N.S.	N.S.	< 110°F	43°C
TDS	N.S.	2 000	N.S.	N.S.
Electr. conductivity (micromhos)	5 000	N.S.	N.S.	N.S.
Suspended Solids	N.S.	600	1 000	N.S.
Sodium (as Na)	N.S.	75	1 000	N.S.
Soap, oil, grease	500	400	400	200
Substances not in solution (incl. fat, oil, grease, waxes, etc.)	2 000	N.S.	N.S.	N.S.
Chlorides	N.S.	N.S.	1 000	N.S.
Free Chlorine	100	N.S.	N.S.	N.S.
Silver (as Ag)	N.S.	Nil	N.S.	N.S.
Iron (as Fe)		N.S.	N.S.	N.S.
Chromium (as Cr)		20	25	20
Copper (as Cu)		20	25	20
Nickel (as Ni)		20	25	20
Zinc (as Zn)		20	25	20
Cadmium (as Cd)		20		20
Arsenic (as As)		N.S.	N.S.	N.S.
Boron (as B)		N.S.	N.S.	N.S.
Lead (as Pb)		N.S.	N.S.	N.S.
Selenium (as Se)		N.S.	N.S.	N.S.
Mercury (as Hg)		N.S.	N.S.	20
Sulphides (as S)	50	20	50	50
Fluorides (as F)	5	N.S.	N.S.	N.S.
Formaldehyde	50	N.S.	N.S.	N.S.
Cyanides (as CN)	20	10	20	10
Total sugars and starch	1 500	N.S.	1 000	N.S.
Tar and tar oils insoluble in water	N.S.	60	50	50
Calcium carbide	Nil	Nil	Nil	Nil
Total sulphates	1 800	300	500	200

*Specifications for Germiston are presently under revision.

N.S. denotes not specified.

Typical analyses of effluents from electroplating plants as found during a survey in the Johannesburg area, are given below (in mg/l, except pH):

pH	2.6 - 12.5
TDS	200 - 22 700
Sulphates	20 - 3 200
Chlorides	5 - 1 600
Sodium	5 - 1 000
Cadmium	Traces - 6
Chromium	Traces - 300
Copper	Traces - 110
Iron	Traces - 5 000
Lead	Traces - 6
Nickel	Traces - 200

The dumping of untreated steel pickle liquors and of untreated electroplating wastes with their high concentrations of metals contravenes the set effluent standard and is, therefore, illegal.

From the Rondebult sewage works, serving the Germiston/Alberton district, there is a case on record where 2 000 mg/l Zn was found in the sewer pipe from Alberton after dilution with domestic sewage. The slug dose of Zn in the industrial discharge, presumably from a galvanising plant, was, therefore, even more concentrated. From Krugersdorp it is reported that, on a few occasions, slugs of up to 700 mg/l chromium have reached the local sewage works.

In Pretoria West about five years back one factory was responsible for the discharge into the sewer of 990 kg of copper and about 350 kg Zn per month. This quantity was contained in only about 15 000 gallons (67 m³) of concentrated waste liquor, whereas the total effluent, rinse water included, was 2 mil. gal/month (9 100 m³).

Naturally, metal concentrations of this order are toxic to the micro-biological life in sewage purification works and can seriously affect the performance of the works. The toxicity of metals in solution is furthermore aggravated if the metals are present in the form of cyanides, as is often the case with electroplating wastes. Therefore, effluent drainage regulations of most municipalities demand the complete oxidation of metal/cyanide complexes to prevent the formation of highly toxic cyanic acid by hydrolysis or dissociation, and to enable the best removal of the metal by precipitation as hydroxides. This aspect must also be considered for the future reclamation of high-class water for unrestricted use from municipal sewage.

Remedial measures to curb pollution from metallurgical processes

In steelmaking, the disposal of *by-products from coke-ovens* presents a serious problem. The volume of effluent per ton of coal carbonised amounts to about 80 gallons ammoniacal liquor, and 30 gallons phenolic by-products. Iscor-Pretoria produces 420 000 gallons of this liquor per day. Investigations into biotreatment of this liquor by activated sludge had shown that the oxidation of ammonia at concentrations of 300-400 mg/l by the *nitrobacter* or *nitrosomonas* organisms did not give satisfactory results.

The problem at Pretoria was solved by using the coke-oven effluent for coke quenching, thereby replacing an equivalent volume of clean water. Contrary to results in Great Britain and elsewhere, only minor additional corrosion of equipment was detected. This is attributed to the very low chloride content of about 70 mg/l in

the ISCOR coke-oven liquor as compared with those overseas which may contain up to 5 000 mg/l.¹⁴

Dust of submicron size, as it originates from blast or open hearth furnaces, can be removed by electrostatic precipitation or by high energy wet scrubbing. When using the latter method, elimination of air pollution may result in water pollution, since the dust particles cannot be removed completely in a clarifier of practical size. The underflow from the clarifier is pumped to vacuum rotary filters for dewatering. Aluminium sulphate or other flocculants are often used to aid settling.

Fluorides in waste waters can often be treated satisfactorily by neutralization with lime and sedimentation in clarification units at pH values between 8 to 11. Where required, additional fluoride removal may be obtained by passing the fluoride waste through a bed of activated alumina treated with sulphuric acid.

The handling of oil and oil emulsions is of specific importance to the metal industry.

Waste oils may have a specific gravity greater than 1.0 or may be lighter than water. High temperature coke-oven tar oil fractions which distil over at temperatures about 180°C are heavier than water. This fact must be known when using an oil intercepting tank. A few designs of oil separators commonly used by industry are shown in Fig. 3 and 4.

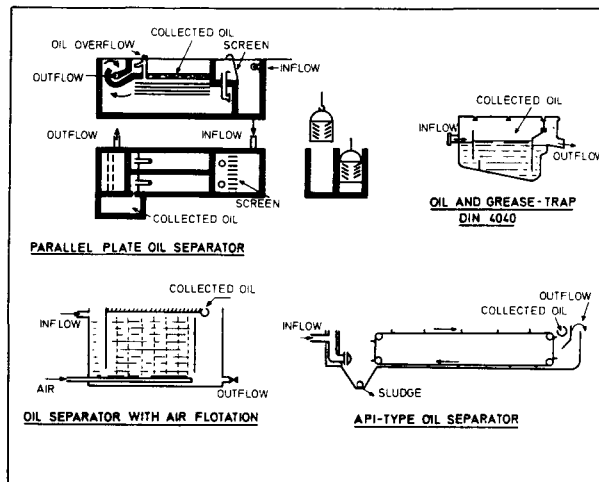


Fig. 3—Oil separators as used in industry.

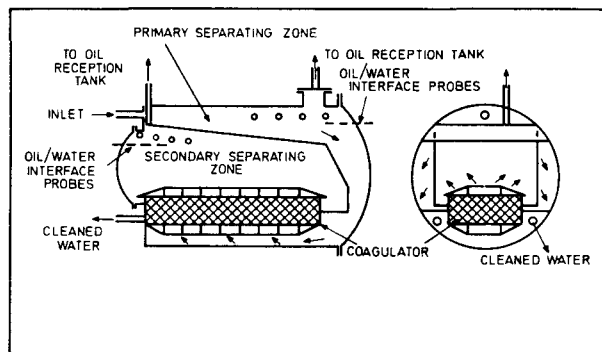


Fig. 4—Oily water separator for oils with a density close to that of water.

The treatment of oil emulsions arising from engineering workshops consists of breaking the emulsion followed by mechanical separation of the oil and aqueous phase. Demulsifying agents may be sulphuric acid, aluminium sulphate, ferrous sulphate, calcium chloride, polyelectrolytes and other chemicals. Dilute acid rinse water and spent pickle liquor are used successfully. Batchwise treatment is preferred for optimum demulsification. Heating to 80°-90°C assists in the separation of the oily layer. The batchwise and continuous separation of oil from waste oil emulsion is shown in Fig. 5.¹⁵

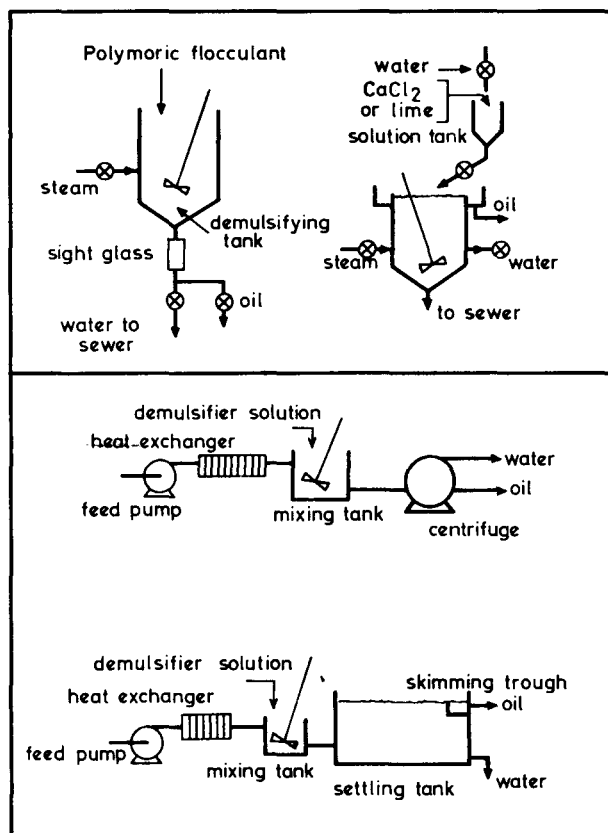


Fig. 5—Batchwise and continuous separation of oil from waste oil-emulsion.

Centrifuging is another way to separate oil and water, whereas adsorption onto activated carbon is efficient but too expensive.

Steel pickling to remove oxide scales is usually carried out with 25-30 per cent H_2SO_4 . Due to the formation of $FeSO_4$, it is not possible to use the acid completely; when the concentration of the free H_2SO_4 has dropped to 7-8 per cent, the spent acid must be removed, otherwise the formation of $FeSO_4$ crystals would interfere with the pickling. For the treatment of pickling effluents, there are three types of treatment available which are discussed here:

(i) *Neutralisation with lime*

The disadvantage is that large quantities of sludge, mainly $CaSO_4$, are formed which create another disposal problem, similar to that encountered with neutralisation of acid mine drainage. The neutralised effluent contains large concentrations of partly soluble ferrous hydroxide which has to be oxidised

by aeration to ferric hydroxide for removal by precipitation (see Fig. 2). No saleable by-products are recovered, all acid used in pickling is completely lost, and the treated effluent, owing to its high concentration of dissolved solids, is unsuitable for re-use.

(ii) *Removal of Ferrous Sulphate by crystallisation*

With this process it is possible to reuse the fraction of free spent acid which is left over after the removal of $FeSO_4$. Addition of fresh H_2SO_4 is required to replace the loss of fixed acid which has been withdrawn with the $FeSO_4$ crystals. A great problem is the disposal of the crystallised $FeSO_4 \cdot 7 H_2O$ which is usually recovered in quantities exceeding the demand.

(iii) *Complete regeneration of the spent pickle liquor*

This is the newest development applicable for both the H_2SO_4 and hydrochloric acid (HCl) pickle acids. The core of this process is the high-turbulence reactor. Conversion of the sulphurdioxide (SO_2) gas from such reactors back into sulphuric acid is not economic on a small scale. Recovery of HCl vapours from the reactor into liquid HCl is, however, economically possible for the small-scale operator and is the reason for the fact that HCl pickling is now rapidly being adopted in the steel industry. Fuel oil and air are required to heat the spent acid to the reaction temperature of 500-800°C. The dissolved iron is roasted to produce ferric-oxide (Fe_2O_3), whereas the HCl vapours are passed via an electrostatic precipitator into an acid absorber which is essentially a packed column in which the HCl vapours are condensed by addition of cold water. HCl losses are of the order of one per cent of the acid in circulation. The only effluent consists of surplus rinse water in excess of the volumes used for HCl absorption which, after neutralisation, is discharged into the sewer. The recovered Fe_2O_3 is used by steelworks or as pigment by the paint industry. The layout of an HCl regeneration plant is shown in Fig. 6.

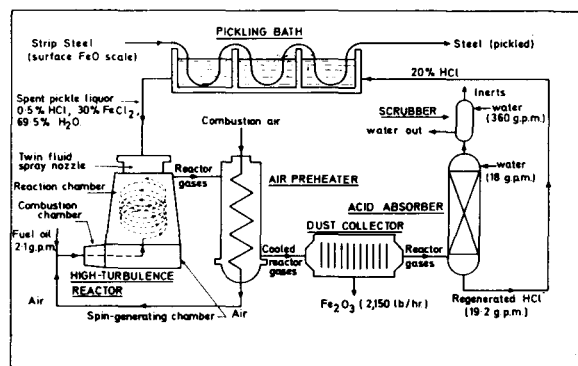
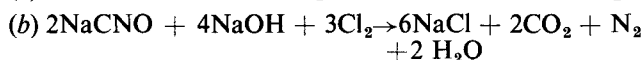
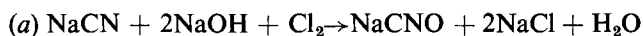


Fig. 6—HCl-regeneration from spent HCl Pickle liquor (System Dr C. Otto & Co.).

Among the practical applications of ion-exchange processes in the treatment of waste water is the recovery of copper, aluminium and nickel from electroplating wastes, and of uranium in the uranium production process. Copper from more concentrated waste flows can also be recovered by cementation onto iron filings or by the electrolytic process to recover cathodic copper.

Cyanides are destroyed by oxidation at pH values above 10, usually by chlorine. The oxidation may be

carried to either cyanate or to carbon dioxide and nitrogen, according to the following reactions:



Reaction (a) is almost instantaneous being 80-90 per cent complete in two minutes; about 2.7 kg of Cl_2 and 3.1 kg of NaOH are required for each kg of cyanide.

Reaction (b) is slower, about one hour, and the chemicals required (theoretical) are 6.8 kg of Cl_2 and 7.3 kg of NaOH per kg of CN^- . In actual practice it has been found that 8 kg of Cl_2 is required for the complete oxidation per kg of CN^- .¹⁶

Chromic acid is one of the pollutants which may find its way into the sewer system as a concentrated slug, either by accidental discharge owing to cracking of the tank, or accidental syphoning out through pipes left in the bath for plating, or by deliberate discharge after spoiling the chromic acid by HCl from pickling. Regeneration of chromic acid is often regarded as impractical for cost reasons.

The treatment for chromic acid consists generally of reduction from the hexavalent to the trivalent state at a pH of 2-3 by SO_2 , by soluble sulphite or by ferrous sulphate, followed by precipitation in a lime treatment tank. This leaves the operator with a sludge handling problem.

Chromates can also be removed by weak base anionic-exchange resins which retain strong acid radicals such as SO_4^{--} , Cl^- , CrO_4^{--} . Regeneration of the retained chromate requires another cation-exchange resin for conversion into chromic acid. Equipment and chemical costs are high and, as it is cheaper to use fresh chromic acid rather to recover the chromium, ion-exchange has not become a generally accepted method for chromium recovery, as in the case of Ni, Al or Cu.¹⁷

For *rinse water reclamation*, however, to provide closed circuit rinsing, demineralisation by ion-exchange has been adopted by a number of larger metal finishing plants. Resin combinations vary with the waste flow. One large operator employs the following equipment as shown in Fig. 7:

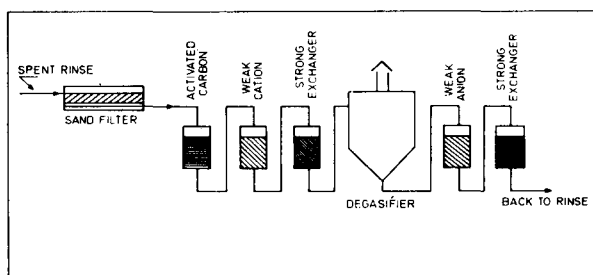


Fig. 7—Demineralization plant for rinse water reclamation.

- (i) rapid sand filter to retain coarse materials;
- (ii) activated carbon filter to remove detergents;
- (iii) weak base cationic-exchange resin to retain metals present as bicarbonates;
- (iv) strong base cationic-exchange resin to retain metals present as sulphates, chlorides;
- (v) degasifier to remove CO_2 and to save chemicals for regeneration of anionic resin-exchanger;
- (vi) weak base anionic-exchange resin to retain sulphates and chromates; and

(vii) a strong base anionic-exchange resin to retain cyanides or silicates.

The reclaimed rinse water is aggressive owing to the absence of Ca- and Mg-salts and has, therefore, to be conveyed in acid-resistant PVC pipes to neoprene-lined equipment. About 95-98 per cent of the water passing through the system is recovered for reuse. The old concept of effluent treatment in electroplating without water renovation and the new concept with rinse water reclamation are shown by Fig. 8 and 9.

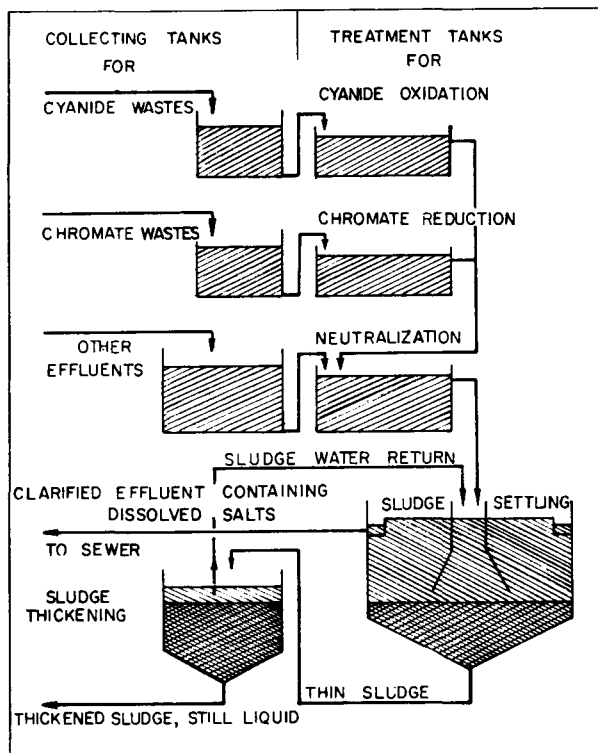


Fig. 8—Electroplating plant: effluent treatment without water renovation.

CONCLUSIONS

A great deal of knowledge has been accumulated in the past on the adverse effects of effluents from mining and metallurgical industries, on how they originate, and on methods to counteract these pollution effects. Especially the problems encountered with mine effluents are of such complexity and magnitude that they cannot be solved satisfactorily without the concerted efforts of mines, local, regional and governmental authorities. Such action indeed will inevitably lead to cutting down the interference of mineral pollution with fresh water environment to practical proportions.

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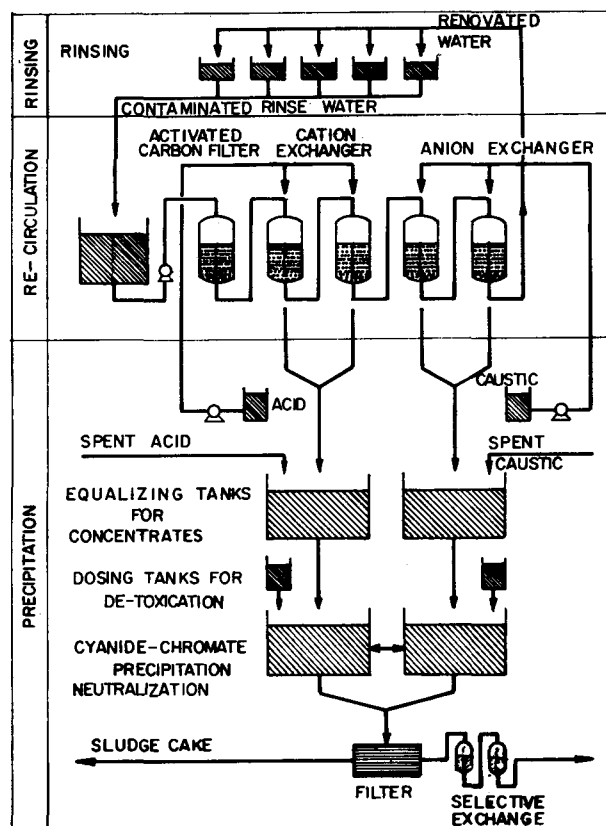


Fig. 9—Rinse water renovation by ion-exchange in a metal-finishing plant.

Discussion

Dr C. M. van Staden (Fellow): Mr President, ladies and gentlemen, thank you very much for this opportunity to contribute to the paper by Dr Stander, and Messrs Henzen and Funke.

First of all, my congratulations to Dr Stander on being re-elected President of the International Association of Water Pollution Research. We in South Africa are proud that this honour was again bestowed on our leading scientist in the field of water research. Furthermore, my congratulations to the authors of this paper.

The growth of the pollution problem caused by acidic water discharged from abandoned collieries, is known to most of us. However, I am not aware of any case where an abandoned gold mine is directly discharging polluted underground water. I think it is also a debatable point as to what the quality of underground water being discharged from abandoned gold mines would be in the long run. Any reduction works on a gold mine which practises only fairly good housekeeping, should not cause any water pollution by cyanide.

First of all, any cyanide solution before gold precipitation would be too valuable to lose. Secondly, the precipitated solution, which contains the cyanide, is used to pump slime to slimes dams. Any cyanide pollution that

may occur at the slimes dam, must come from the top and, fortunately, the days when penstock water was discharged directly from the top of dams into public streams, have gone. Run-off and seepage is usually acidic, thus decomposing the cyanide.

The code of practice by the Chamber of Mines is quite clear on the point as to how the tops of dams should be secured, to prevent any process water or storm-water polluting public streams. The general standards are given on page three of the paper.

To my knowledge, under certain circumstances a degree of relaxation can be given regarding the faecal coli count; namely a permissible count of 1 000 per 100 ml. I feel very strongly that research aimed at inhibiting the activity of acid-producing bacteria should be encouraged. Success in this field would be of great benefit to the mining industry.

I am very thankful that the authors have mentioned vegetation of dumps as a method to combat water pollution, with the full awareness that the key objective in vegetating dumps is to prevent air pollution. A problem that I have not heard mentioned before and on which I would appreciate the views of the authors, is the pollution that may be caused by power-stations discharging