A biological process for sulphate removal from industrial effluents

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Abstract

A biological process comprising anaerobic, stripping and aerobic stages is described for the treatment of effluents containing excessive amounts of calcium sulphate and high concentrations of heavy metals. By using molasses as carbon source in an upflow anaerobic packed bed reactor, sulphate was reduced to hydrogen sulphide, which precipitated heavy metals as the corresponding sulphides. The removal of the end products of the anaerobic stage, namely hydrogen sulphide, calcium carbonate and soluble organic matter, was studied under batch conditions by applying air stripping, clarification and aerobic treatment consecutively.

Approximately 90 per cent of the influent sulphate was removed at a hydraulic retention time of 10 h when 3 g molasses per ℓ effluent was dosed. The final product was free of heavy metals and cyanide while the COD value of the effluent was 300 mg/ℓ. The carbonaceous residual consisted of phenol which originates from the molasses, but which is harmless to most of the mining metallurgical processes. One of the attractive features of the process is that sulphur may be recovered as a by-product from effluent purification.

Introduction

The mining industry is having to reuse water to an increasing extent due to the rising cost of water and the strict quality standards covering effluent discharge into water-courses. Of particular concern are effluents which contain calcium sulphate, usually to saturation levels, in addition to cyanide and organics. Seeded slurry reverse osmosis is a viable treatment method but leaves a brine solution which requires further treatment (Harries, 1985). This paper is concerned with biological sulphate reduction, which is an alternative treatment method.

Various researchers have studied biological sulphate reduction in the past. Middleton and Lawrence (1977) determined the kinetics of microbial sulphate reduction in a complete mix reactor using acetic acid as carbon source and observed a sulphate reduction rate of 0,29 g $SO_4/\ell.d$ (biomass concentration was not specified). Cork and Cusanovich (1978) developed a continuous purge system, using an inert carrier gas (75% argon and 25% CO_2), to feed sulphide removed from actively growing cultures of *Desulfovibrio desulfuricans* to *Chlorobium thiosulfatophilum*, for oxidation to sulphur. A sulphate reduction rate of 6,3 g $SO_4/\ell.d$ was observed in a completely mixed reactor containing 12 600 mg/ℓ lactic acid, at pH 6,5 and temperature 30°C (biomass concentration was not specified). Some 91% of the hydrogen sulphide produced was swept off into a sulphide oxidizing chamber containing *Chlorobium*, where 88% was converted to sulphur. This represents an overall sulphur yield of 80%.

Maree and Strydom (1985) studied sulphate reduction and heavy metal removal in an upflow anaerobic packed bed reactor, using sugar, sewage sludge and the effluent of a sulphite pulp mill as carbon sources. No information, however, is available on what further treatment steps are required to produce a water of reusable quality after anaerobic sulphate removal has been applied.

This study was aimed primarily at determining the treatability of a gold and uranium plant effluent in an upflow anaerobic packed bed reactor, and identification of the stages required for removal of end-products such as hydrogen sulphide, calcium carbonate and soluble organic carbon.

Experimental

The experimental work was divided into two phases. The sulphate reduction stage was studied under continuous conditions, while the removal of the end products of this stage, namely hydrogen sulphide, calcium carbonate and soluble organic matter, was investigated under batch conditions by applying air stripping, clarification and aerobic treatment consecutively.

Continuous-flow reactor

A schematic diagram of the laboratory-scale plant used is given in Figure 1. The anaerobic packed bed reactor was manufactured from Perspex to allow visual inspection of the interior of the reactor. The bottom of the column was tapered to facilitate fluidization of the medium when flushing out dead bacteria. This was done once a week at an upflow velocity of 50 m/h, achieved by increasing the recirculation rate. The distribution chamber served as a reservoir for recirculating liquid and was equipped with an overflow to dispose of the effluent. A recirculation rate of 100 ℓ/d (compared with the inflow rate of 2 ℓ/d) was maintained to approach conditions similar to those of a completely mixed reactor.

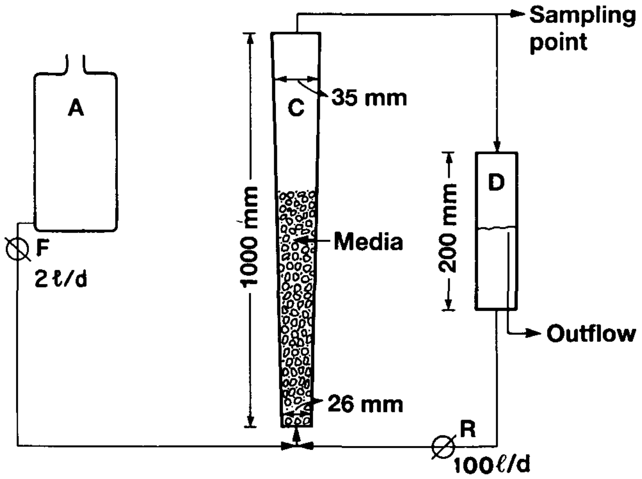

Figure 1
Schematic diagram of laboratory-scale plant used for biological sulphate reduction.

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TABLE 1
CHEMICAL COMPOSITION OF RAW AND TREATED WATER

Determinand	Unit	Raw	Raw and molasses	Treated
pH		7,2	7,0	7,3
Conductivity	(mS/m)	390	400	380
Kjeldahl nitrogen (as N)	(mg/ℓ)	12,5	12,8	11,2
Ammonia nitrogen (as N)	(mg/ℓ)	11,4	11,5	4,0
Nitrate nitrogen (as N)	(mg/ℓ)	2,5	2,8	1,2
Nitrite nitrogen (as N)	(mg/ℓ)	0,1	0,2	0,1
Sulphate (as SO_4)	(mg/ℓ)	2 600	2 600	163 ± 69**
Free Sulphide (as SO_4)	(mg/ℓ)	0	0	451 ± 144**
Total phosphate (as P)	(mg/ℓ)	1,5	1,5	1,5
Orthophosphate (as P)	(mg/ℓ)	0,5	0,5	0,5
Chloride (as Cl)	(mg/ℓ)	236	316	338
Total alkalinity (as $CaCO_3$)	(mg/ℓ)	40	40	2 174 ± 222**
COD (as O_2)	(mg/ℓ)	40	3 000	854
COD and Sulphide (as O_2)	(mg/ℓ)	40	3 000	1 155 ± 206**
Sodium (as Na)	(mg/ℓ)	246	284	276
Potassium (as K)	(mg/ℓ)	50	160	168
Calcium (as $CaCO_3$)	(mg/ℓ)	1 780	1 780	1 600 ± 185**
Magnesium (as Mg)	(mg/ℓ)	175	204	186
Silicon (as Si)	(mg/ℓ)	4,0	4,7	11,3
MBAS (as LAS)	(μg/ℓ)	524	1 543	2 074
Aluminium (as Al)	(μg/ℓ)	54	270	143
Boron (as B)	(μg/ℓ)	285	947	1 641
Fluoride (as F)	(μg/ℓ)	643	645	470
Arsenic (as As)	(μg/ℓ)	3	6	3
Chromium (as Cr)	(μg/ℓ)	0	0	0
Cadmium (as Cd)	(μg/ℓ)	14	15	4
Cobalt (as Co)	(μg/ℓ)	942	986	401
Copper (as Cu)	(μg/ℓ)	59	300	9
Gold (as Au)	(μg/ℓ)	109	116	60
Iron (as Fe)	(μg/ℓ)	207	5 860	272
Lead (as Pb)	(μg/ℓ)	162	199	53
Mercury (as Hg)	(μg/ℓ)	3	3	2
Manganese (as Mn)	(μg/ℓ)	2 280	2 990	246
Nickel (as Ni)	(μg/ℓ)	1 550	1 304	146
Silver (as Ag)	(μg/ℓ)	0	0	0
Zinc (as Zn)	(μg/ℓ)	74	40	49
Cations	(me/ℓ)	63,0	70,1*	64,9*
Anions	(me/ℓ)	61,8	64,1*	64,2*

Note: Each value represents mean value of 5 determinations except **
*The difference between the cation and anion totals is due to the fact that organic anions have not been taken into account.
**Mean values with standard deviations of 30 determinations.

A Masterflex peristaltic pump was used for recirculation purposes and a Heidolph peristaltic pump for introducing the influent. The bottom half of the anaerobic reactor was filled with dolomitic pebbles, with a diameter of 2 to 3 mm. The void ratio of the medium was 50%. Feedstock, which was stored at 4°C, consisted of process water with composition as shown in Table 1, supplemented with 3 mℓ molasses per ℓ (COD value of raw molasses is 1 000 g/ℓ.) Molasses was used as it is considered to be the most economical carbon source available for large-scale application. A biologically active film was established on the stone medium by inoculating the reactor with activated sludge from a laboratory activated sludge plant.

Batch studies

Hydrogen sulphide stripping was studied in batch systems by aerating 20 ℓ portions of anaerobically treated water, gathered over a period of 20 days, for 10 h. The calcium carbonate-rich colloidal suspension, obtained after air stripping, was clarified by using ferric chloride as coagulant. The optimum dosage required for this purpose was determined by adding ferric chloride to concentrations between 0 and 500 mg/ℓ (as $FeCl_3$) in 500 mℓ aliquots of the anaerobically treated water, followed by rapid mixing (two min), slow mixing (eight min) and settling (ten min), whereupon unfiltered and filtered samples were drawn for analysis.

Aerobic treatment was conducted batchwise, after supplementing process water with ammonia-N, phosphate-P and cyanide-CN, to concentration levels of 20, 4 and 20 mg/ℓ respectively. Cyanide was added because it often is a pollutant in gold mining effluents, and because it was necessary to study its biodegradability in this process. Bacterial growth was initiated by adding 200 mg/ℓ settled activated sludge with a suspended solids concentration of 5 500 mg/ℓ. Air was supplied at a constant rate through a diffuser to maintain a dissolved oxygen concentration of 4 mg/ℓ. The sludge was allowed to settle daily, upon which 600 mℓ of the supernatant was replaced with the same volume of stored water (also supplemented with ammonia, phosphate and cyanide).

Analytical

In the continuous-flow reactor samples were taken daily from the distribution chamber and analyzed for sulphate, sulphide, alkalinty, COD and pH. Complete chemical analyses were performed on the influent and effluent water after steady state operation had been obtained. Manual determinations of sulphate, COD, alkalinity, sulphide and pH were carried out on filtered samples according to analytical procedures as described in Standard Methods (American Public Health Association, 1965). Direct flame atomic absorption and automatic colorimetric techniques were used for the other chemical determinations. The COD value obtained was corrected by subtracting the COD equivalent of the sulphide content in the water (96 mg sulphate equivalent to 64 mg COD).

During batch experimentation, samples were analysed for sulphide, sulphate, calcium, alkalinity and pH while studying hydrogen sulphide stripping; turbidity and pH while studying clarification; and COD, calcium, alkalinity, sulphate, sulphide, cyanide and pH while studying aerobic treatment. Analyses on turbidity, sulphide and pH were done on unfiltered samples while the rest were done on filtered samples.

Results and discussion

Anaerobic treatment

The various reactions that take place in this stage will be discussed separately in the following paragraphs:

Fermentation

Sulphate reducing bacteria utilize fermentation products as their carbon source (Jørgensen, 1982), and could also live symbiotically with fermentation organisms, such as *Lactobacilli*, when molasses is provided as carbon source (Lebel *et al.*, 1985). The conversion of the sugar content of molasses to lactate, which is required for anaerobic respiration purposes, could thus be represented by the following reaction:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4CH_3CHOHCOOH \qquad (1)$$

Anaerobic respiration

Sulphate reducing bacteria, such as *Desulfovibrio desulfuricans*, use fermentation products, such as lactate, to produce acetate according to the following reaction (Cork and Cusanovich, 1979):

$$2CH_3CHOHCOO^- + SO_4^= \rightarrow 2CH_3COO^- + 2HCO_3^- + H_2S \qquad (2)$$

Reaction (2) can also be written as follows

$$2C + SO_4^= + 2H_2O \rightarrow H_2S + 2HCO_3^- \qquad (3)$$

This shows that 96 g sulphate reacts with 64 g organic carbon (expressed as COD) to produce 96 g sulphide and 100 g alkalinity (as $CaCO_3$). Experimentally, 2 403 mg sulphate consumed 2 146 mg COD in the anaerobic reactor to produce 451 mg sulphide (as SO_4) and 2 134 mg alkalinity (as $CaCO_3$) (Table 2).

Table 2 shows that the theoretically expected change in COD concentration was 1 602 mg/ℓ (reaction (3)) whereas experimentally 2 146 mg/ℓ was found. This discrepancy can be ascribed to the following factors:

- fermentation of long-chain organic molecules (reaction (1); and
- production of bacterial cells.

TABLE 2
COMPARISON BETWEEN EXPERIMENTAL AND THEORETICAL CHANGES IN CONCENTRATIONS OF VARIOUS PARAMETERS DURING SULPHATE REDUCTION (RESULTS IN mg/ℓ)

Determinand	Theoretical*	Experimental	Theoretical**
Sulphate (as SO_4)	96	2 403	2 403
Sulphide (as SO_4)	96	451	2 403
Alkalinity (as $CaCO_3$)	100	2 134	2 503
COD	64	2 146	1 602

*Figures obtained from Equation 3
**Figures under * multiplied by 2 403/96.

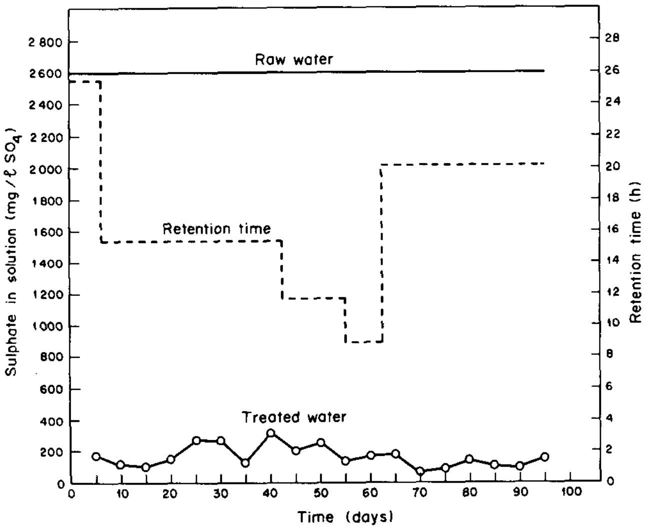

Figure 2
Temporal variation of sulphate concentration during biological treatment.

The results in Table 2 show that less sulphide was produced than expected from equation (3), a fact which indicates that sulphide was partially removed in the process. The difference of 1 952 mg/ℓ can be due to one or more of the following three factors:

- heavy metal sulphide precipitation;
- biological sulphide oxidation to sulphur; and
- escape of gaseous hydrogen sulphide.

The results in Table 1 and Figure 2 show that the sulphate present in the specific mining effluent can be reduced from 2 600 mg/ℓ to 200 mg/ℓ in an anaerobic packed bed reactor at nominal HRT as short as 9 h.

Photosynthetic sulphide oxidation

Photosynthetic sulphur bacteria oxidize sulphide to sulphur according to the following reaction (Biebl and Pfennig, 1978):

$$17H_2S + 8CO_2 \xrightarrow{light} 2(C_4H_7O_3) + 17S + 10H_2O \qquad (4)$$

The sulphide produced in the anaerobic reactor is also removed by oxidation to sulphur. The green and purple sulphur bacteria, *Chlorobium* and *Chromatium*, which were visible on the interior of the walls of the perspex reactor, photosynthetically oxidize the formed sulphide to elemental sulphur (Cork and Cusanovich, 1978). *Chlorobium thiosulfatophilum* excretes colloidal sulphur, while *Chromatium finosum* stores sulphur intracellularly.

Heavy metal precipitation

Heavy metals were precipitated as sulphides according to the following general reaction scheme:

$$M^{++} + H_2S \rightarrow MS + 2H^+ \qquad (5)$$

where M^{++} represents Co, Cu, Fe, Mn, Ni or Zn.

The results in Table 1 indicate that the heavy metals cobalt, copper, iron, manganese, nickel and zinc are effectively removed in the anaerobic stage. The heavy metal sulphide precipitate accumulated together with the biomass in the medium of the packed-bed reactor, and was removed by means of back washing at regular intervals. The amount of sulphide utilized during precipitation with heavy metals can be calculated from the following equation:

$$\Delta S = \Sigma\,(\Delta m/_{M}).96$$

where

ΔS = amount of sulphide precipitated (as SO_4)
Δm = amount of Co, Cu, Fe, Mn, Ni and Zn precipitated (as mg/ℓ metal)
M = molecular mass of heavy metal

$$\Delta S = \left(\frac{\Delta Co}{58,9} + \frac{\Delta Cu}{63,5} + \frac{\Delta Fe}{55,8} + \frac{\Delta Mn}{55,0} + \frac{\Delta Ni}{58,7} + \frac{\Delta Zn}{65,4}\right) \times 96$$

$$= \left(\frac{0,59}{58,9} + \frac{0,29}{63,5} + \frac{5,59}{55,8} + \frac{2,74}{55,0} + \frac{1,16}{58,7} + \frac{0,33}{65,4}\right) \times 96$$

$$= 18,2 \text{ mg}/\ell \text{ sulphide (as } SO_4)$$

TABLE 3
QUALITY OF WATER BEFORE AND AFTER HYDROGEN SULPHIDE STRIPPING (RESULTS IN mg/ℓ)

Determinand	Before	After
Sulphide (as SO_4)	500	85
Calcium (as $CaCO_3$)	1 344	660
Alkalinity (as $CaCO_3$)	1 524	820
Sulphate (as SO_4)	426	420
pH	7,0	8,1

The metals with high metal sulphide solubility products, namely the alkali-earth metals (calcium and magnesium) and alkali metals (sodium and potassium) are only slightly influenced by the sulphide present in the anaerobic stage. The fact that heavy metals are efficiently removed in this process is an indication that peaks of heavy metal concentrations in industrial effluents will not easily disturb the biological activity. This statement, however, needs further verification.

Calcium carbonate crystallization

Calcium carbonate crystallization occurs according to the reaction

$$Ca^{++} + CO_3^{=} \rightarrow CaCO_3 \qquad (6)$$

The observed increase in alkalinity (2 134 mg/ℓ as $CaCO_3$) was less than the 2 503 mg/ℓ expected from equation (3) (Table 2). The difference is mainly due to calcium carbonate crystallization (equation (6)). Calcium is present in the feed water, while carbonate originates from carbon dioxide which is produced as a by-product during fermentation and anaerobic respiration.

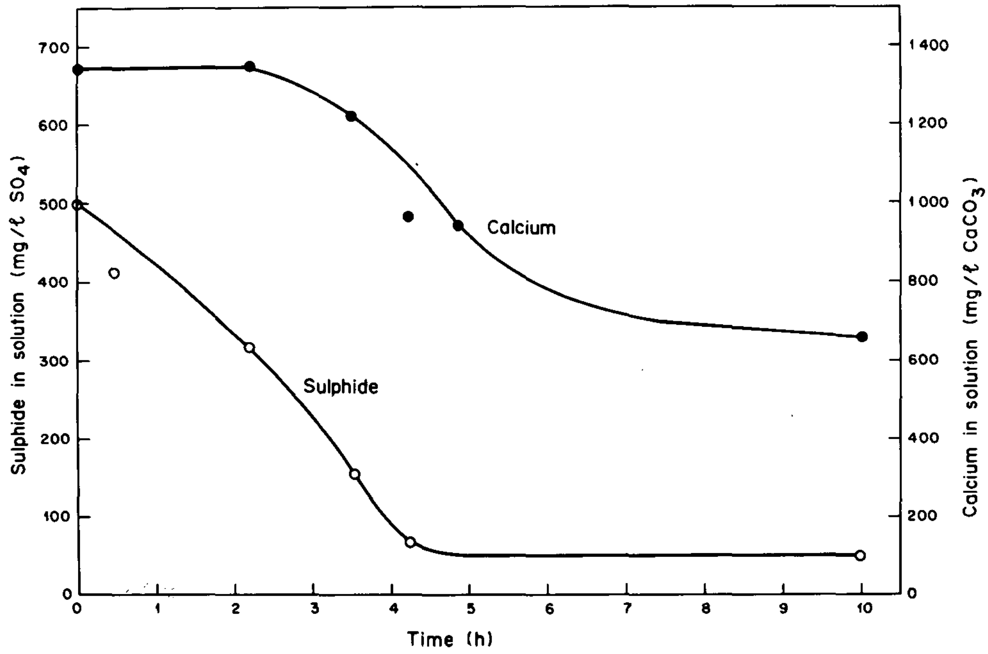

Figure 3
Influence of air stripping on the removal of sulphide and calcium in solution.

Removal of end products

During a 6 h aeration period of the anaerobically treated water, both sulphide and calcium carbonate were removed from solution to levels of 80 mg/ℓ (as SO_4) and 660 mg/ℓ (as $CaCO_3$) respectively (Figure 3 and Table 3). The fact that calcium carbonate crystallization took place only after sulphide removal can be ascribed to the lower solubility of calcium carbonate at the increasing pH values, accompanying hydrogen sulphide stripping.

About 500 mg/ℓ ferric chloride was required to decrease the turbidity of the water following H_2S stripping, due mainly to colloidal $CaCO_3$, from 215 to 19 NTU (Table 4). The use of ferric chloride is not advocated as unwanted chloride ions are added to the water. A sulphate salt, such as ferric sulphate, would be preferable as the sulphate can be removed in the process in case of closed circuit water treatment systems. Current tests show that the calcium carbonate suspension flocculates together with the biomass when aerobic treatment is applied directly after anaerobic treatment.

The results in Table 5 show that the COD decreased from 1 128 to 300 mg/ℓ, during aerobic treatment, which indicates that organic molecules such as acetate were converted to bicarbonate. The carbonaceous residual consisted of phenol, which is harmless to most of the mining metallurgical processes. The nutrients (ammonia and phosphate) supplied in the feedstock were completely utilized for cell synthesis and/or nitrification. The decrease in the calcium and alkalinity values indicates that calcium carbonate crystallization occurred. Total cyanide was removed to the extent of 97%, which is a result of biodegradation or air stripping. This finding is in accordance with that of Rapean *et al.* (1980) who obtained 98% cyanide removal from a solution initially containing 8 mg/ℓ (as CN) during treatment in an activated sludge plant at a retention time of less than five days.

TABLE 4
DETERMINATION OF OPTIMUM FERRIC CHLORIDE DOSAGE FOR COAGULATION OF EFFLUENT FOLLOWING H_2S STRIPPING

Determinand	FeCl$_3$ dosage (mg/ℓ FeCl$_3$)					
	0	80	200	300	400	500
pH	7,7	7,3	6,9	6,5	5,9	5,7
Turbidity (NTU)	215	140	95	83	48	19

Economic considerations

The practical applicability of a process ultimately depends on its economics. The most costly item of this process is the organic carbon source, namely molasses. Approximately 2,9 mℓ (3,9 g) molasses syrup is required to remove 2 600 mg sulphate. Accepting the price of molasses as 8c/kg, this cost alone would amount to 31c/m³ to treat water containing 2 600 mg/ℓ sulphate. By using waste carbon sources such as sewage sludge, the treatment cost would be less (Maree and Strydom, 1985).

TABLE 5
QUALITY OF WATER BEFORE AND AFTER AEROBIC TREATMENT (RESULTS IN mg/ℓ)

Determinand	Before	After
pH	7,2	8,3
COD (as O_2)	1 128	303
Sulphate (as SO_4)	510	530
Alkalinity (as $CaCO_3$)	520	200
Calcium (as $CaCO_3$)	1 290	880
Sulphide (as SO_4)	0	0
Phosphate (as P)	4	0,3
Kjeldahl nitrogen (as N)	23,0	9,8
Ammonia (as N)	20	0,4
Nitrate (as N)	0	7,5
Total Cyanide (as CN)	24,2	0,58
Free Cyanide (as CN)	9,2	0,06

Conclusions

- During anaerobic treatment, the sulphur species composition of mining effluent was reduced from 2 600 mg/ℓ sulphate to 200 mg/ℓ sulphate (as SO_4), 450 mg/ℓ sulphide (as SO_4), elemental sulphur and metal sulphides. Heavy metals were completely removed while calcium carbonate reached supersaturation due to the presence of a component of molasses which inhibits crystallization.

- The end products of the anaerobically treated water, namely hydrogen sulphide, calcium carbonate and soluble organic carbon, were successfully removed by applying H_2S stripping, clarification and aerobic treatment. Calcium carbonate crystals and other suspended solids were removed by dosing 500 mg/ℓ ferric chloride as coagulant. Gaseous hydrogen sulphide content was decreased to 50 mg/ℓ (as SO_4) and the COD value to 300 mg/ℓ. Cyanide was also removed during aerobic treatment.

- The molasses cost amounts to 31c/m³ when water with a sulphate content of 2 600 mg/ℓ is treated.

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