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(54) TREATMENT OF BRINE TO RECOVER MERCURY

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the treatment of waste brine from a mercury cell.

Waste brine from mercury cells usually contains dissolved chlorine together with mercury in amounts of up to 20 mg/l. Considerable cost savings can be made if the mercury can be effectively recovered.

In our Specification No. 916,866 we have described a process for removal of mercury from waste brine in which mercury is precipitated as mercuric sulphide by adding a source of sulphide ions, together with an alkali to ensure that the sulphide is precipitated in a neutral or alkaline medium. This process produces a precipitate which is very finely divided and difficult to remove.

We have now found that mercury can be effectively removed from waste brine using a mixed media filter to remove a mercuric sulphide precipitate which has been formed without the necessity of ensuring a neutral or alkaline medium.

Thus, according to the invention, there is provided a process for the removal of mercury from chlorine-containing waste brine from a mercury cell which comprises adding sulphide or hydrosulphide ions to the brine in sufficient amount to produce a redox potential of the brine, relative to a saturated KCl-Calomel electrode, of a value more negative than +0.45 volts, preferably +0.25 volts, whereby mercury sulphide is precipitated; and removing the precipitated mercuric sulphide by passing the brine downwards through a filter which comprises at least two directly-superimposed layers of granular filtration material, the average size of the particles of granular material in the

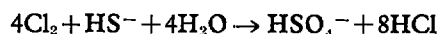
successive superimposed layers decreasing and the specific gravity of the granular material increasing, from the top of the filter downwards.

Usually the precipitate is removed from the filter by backwashing with a liquid, generally water, and preferably also by scouring with a gas, generally air. Preferably the gas is blown upwards to dislodge adherent solids from the filter materials and then the liquid is passed upwards through the bed to fluidise it and remove the precipitate from it. Generally, after the precipitate has been removed, the liquid flow rate is decreased in stages until the bed has settled back substantially to its original form. Since the specific gravity of at least two superimposed layers of the media increases from top to bottom, the rate of settling also increases from top to bottom with the result that the lower layers settle more rapidly than the higher layers and the original structure of the filter is substantially retained.

The backwash liquor is allowed to stand and the precipitate settles rapidly since it is usually a well coagulated coarse and dense solid which can easily be separated from the supernatant liquid by any convenient means.

Metallic mercury can be recovered from the precipitate by any convenient means, for instance by heating with, for example, iron or lime or by dissolving in an alkaline sulphide solution and reducing the solution electrolytically or with a reducing agent, for example sodium amalgam.

It is desirable to remove as much chlorine from the brine as possible, before treatment with the sulphide or hydrosulphide. The brine usually contains about 400 ppm of free chlorine and this may be reduced to as low as 30 ppm by air-blowing. Dechlorination is usually completed by the sulphide or hydrosulphide ions, for example according to equation



[Price 25p]

As a source of sulphide or hydrosulphide ions there is usually used an alkali metal sulphide or hydrosulphide. Sodium hydrosulphide is generally preferred.

- 5 The materials which can be used to make up the filter may be any suitable material as long as in at least two directly superimposed layers the average size of the particles in the successive layers decreases and the specific gravity increases from the top of the filter downwards.

- 10 Examples of suitable materials include anthracite, coal, activated carbon, graphite, quartz, flint, silica, magnesia, alumina, garnet and sand.

- 15 It is preferable that the waste brine is treated to remove insoluble matter, e.g. graphite, before addition of the sulphide or hydrosulphide. This may be carried out by any convenient means, for example by filtration of the brine, e.g. with a filter of the type used to remove the mercuric sulphide precipitate or a precoat filter, such as a precoat charcoal filter. Other additional or alternative means for the insoluble matter removal include using a hydrocyclone. This treatment may be carried out before or after any air-blowing to remove chlorine.

- 20 Although the invention is generally applicable to the treatment of acidic brine the pH is not critical, and it is possible to purify brine having a pH in the range of for example 1 to 11. However it is particularly preferred that during the precipitation the pH is maintained in the range 5 to 7.

- 35 The invention is illustrated in the following Examples in which "ppm" stands for parts per million, weight/volume.

Example 1.

- 40 100 litres of effluent brine from a mercury cell which had been air-blown to reduce the available chlorine to 70 ppm and which contained 10 ppm Hg was passed through a reaction vessel at a rate of 20 litres/hr and treated continuously with sodium sulphide solution to maintain the oxidation potential measured with a platinum electrode and a saturated calomel electrode at +0.1 volt. Mercuric sulphide was precipitated as an extremely fine, black precipitate and was filtered by passing the brine through a 5 cm diameter mixed media filter comprising a 2.5 cm deep top layer of 7—10 B.S. mesh (particle size of 1.7 to 2.4 mm) anthracite having a specific

gravity of 1.4, a 2.5 cm deep intermediate layer of 18—25 B.S. mesh (particle size of 0.6 to 0.85 mm) flint having a specific gravity of 2.65 and a 5 cm deep bottom layer of 30—36 B.S. mesh (particle size of 0.4 to 0.5 mm) alumina having a specific gravity of 3.9. This bed was supported by a 2.5 cm layer of 6—8 B.S. mesh (particle size 2.0 to 2.8 mm) alumina having a specific gravity of 3.9 and a 3.8 cm layer of 0.6 to 1.3 cm diameter pebbles having a specific gravity of 2.7 on a perforated titanium plate. The effluent brine after filtration contained less than 0.1 ppm Hg and no free chlorine.

The precipitate was removed from the bed by passing air upwards through the bed and then passing water upwards through the bed to fluidise it and then remove the precipitate from it. The backwash liquor was collected in a separating funnel and the mercuric sulphide precipitate allowed to settle. The precipitate, which was coarse and dense, settled in a few minutes and was easily separated from the supernatant liquor.

The precipitate recovered from the filter weighed 1.04 g representing 90% mercury recovery.

Example 2.

Effluent brine from a mercury cell, which had been air-blown to reduce the available chlorine to 70 ppm, was passed through two filters in parallel of the type described in Example 1 except that they each had a diameter of 15 cm. The total flow rate through these filters was 1 m³/hr. This filtering reduced the level of insoluble graphite in the brine. The brine was then treated as described in Example 1 to precipitate mercuric sulphide. The brine was then filtered on a filter of the type described in Example 1 except that it had a diameter of 10 cm and each layer of material had a depth of 23 cm. The filtered brine was analysed for mercury content and hence removal efficiency.

The precipitate was removed from the bed by passing air at a pressure of 0.3 to 0.4 kg/cm² gauge upwards through the bed for 2 to 3 minutes. Water at the rate of 8 to 10 litres/minute was then passed upwards to remove the precipitate. The backwash liquor was then collected and analysed for mercury content. The precipitate could easily be removed in a separating funnel.

The results of a number of runs are shown in the following Table.

TABLE

Run No.	Initial concentration of Hg in brine (ppm)	Flow rate through filter (m ³ /hour)	Volume of brine filtered (m ³)	Weight of solids from backwash (g)	Estimated mercury recovery (%)	Removal efficiency half way through run (%)
1	1.8	0.25	19	104	93	96
2	1.8	0.52	11.5	143	96	92
3	1.8	0.25	17.5	138	77	98
4	2.0	0.37	—	—	—	> 95

WHAT WE CLAIM IS:—

1. A process for the removal of mercury from chlorine containing waste brine from a mercury cell which comprises adding sulphide or hydrosulphide ions to the brine in sufficient amount to produce a redox potential of the brine, relative to a saturated KCl-Calomel electrode, of a value more negative than +0.45 volts whereby mercuric sulphide is precipitated; and removing the precipitated mercuric sulphide by passing the brine downwards through a filter which comprises at least two directly superimposed layers of granular filtration material, the average size of the particles of granular material in the successive superimposed layers decreasing and the specific gravity of the granular material increasing, from the top of the filter downwards.

2. A process according to claim 1 in which the redox potential produced is of a value more negative than +0.25 volts.
3. A process according to claim 1 or 2 in which the precipitate is removed from the filter by backwashing with a liquid.
4. A process according to claim 3 in which the bed is also scoured with a gas.
5. A process according to claim 3 or 4 in which the backwashing is carried out using water.
6. A process according to claim 3, 4 or 5 in which the scouring is carried out with air.
7. A process according to any one of claims 3—6 in which scouring is carried out first and then followed by backwashing.
8. A process according to any one of claims 3—7 in which the mercuric sulphide is allowed

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7. A process according to any one of claims 3—6 in which scouring is carried out first and then followed by backwashing.

8. A process according to any one of claims 3—7 in which the mercuric sulphide is allowed



to settle from the backwash liquor and further separated.

- 5 9. A process according to any one of the preceding claims in which the brine is treated to reduce the free chlorine content before treatment with the sulphide or hydrosulphide.

10. A process according to claim 9 in which the chlorine content is reduced by air-blowing.

- 10 11. A process according to any one of the preceding claims in which as a source of sulphide or hydrosulphide ions there is used an alkali metal sulphide or hydrosulphide.

12. A process according to claim 11 in which the source is sodium hydrosulphide.

- 15 13. A process according to any one of the preceding claims in which the filter comprises granular filtration material selected from anthracite, coal, activated carbon, graphite, quartz, flint, silica, magnesia, alumina, garnet and sand.

14. A process according to any one of the preceding claims in which the waste brine is treated to remove insoluble matter before addition of the sulphide or hydrosulphide.

15. A process according to claim 14 in which 25 the waste brine is filtered.

16. A process according to claim 15 in which the waste brine is passed through a filter of the type described in claim 1.

17. A process according to claim 1 substantially as hereinbefore described. 30

18. A process according to claim 1 substantially as hereinbefore described with reference to Example 1.

19. A process according to claim 1 substantially as hereinbefore described with reference to Example 2. 35

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