The following statement is a full description of this invention, including the best method of performing it known to us:

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The present invention relates to a process for the treatment of mercury-bearing wastewater discharged from production facilities where mercury losses occur, particularly from alkaline chloride electrolysis plants.

Mercury losses are inevitably encountered in production facilities where mercury is either processed or used as an auxiliary material. Any mercury collecting on the floor of process plant areas or residual mercury from vessels which are emptied for inspection or maintenance is entrained by flushing water. This flushing water, now called wastewater, consequently contains mercury in varying concentrations, possibly in the order of magnitude of only some ppm, and is discharged to the sewer. It is imperative, indeed, to prevent any mercury emission because mercury in the form of an organic compound, for example methyl mercury, is injurious to the health of any living being. Any quantity of mercury, however small, may enrich in living beings, such as fish, game, and plants and, after conversion to organic mercury, may be injurious to the health of persons who consume such animal or vegetable matter.

In alkaline chloride electrolysis plants, for example, the mercury serves as an auxiliary material. Mercury is the cathode in the electrolysis process and circulates through the cell, the amalgam decomposer, and the mercury pump. Mercury losses which are attributable to leakages on the pumps, the cells or the decomposers or to flushing operations during repair work in the electrolysis plant cannot be avoided. Mercury pumps are normally equipped with water seals for the shafts. Any leak on these seals will permit mercury-bearing seal water to leave the pump.
Inadmissible accumulations of mercury on the cell room floor are removed by periodically hosing down the cell room floor. This way of cleaning the cell room floor is the simplest and cheapest method for removing mercury spills. The mercury entrained by the flushing water is collected in pits which also receive wastewater from other sources which contains metallic mercury, mercury ions, and mercury complexes.

The route so far employed by the industries concerned has been to liberate this water, as far as economically reasonable, from mercury before discharging it to the sewer. Precipitation in the form of mercury sulphide, cementing, ion exchange, and the reduction with hydrazine are among the purification processes applied. For precipitating the mercury in the form of mercury sulphide, sodium sulphide or sodium hydrogensulphide NaHS is added to the mercury-bearing wastewater while maintaining the pH value between 8 and 9; these chemicals cause the mercury to be precipitated as mercury sulphide which is then absorbed at the surface of the flocculated ferric hydroxide through the addition of ferric chloride. After sedimentation of the flocculent, the transparent solution is withdrawn and rejected to the sewer. According to a laboratory report by H.O. Bouveng and P. Ullmann of the "Swedish Water and Air Pollution Research Laboratory" the best result so far obtained is 0.1 ppm at a starting concentration of 3 ppm. The process is intermittent.

Cementing is based on the principle that mercury deposits on the surfaces of base metals because of the different electrochemical potentials. This method requires, however, the use of a cementing column which needs periodic regeneration. The same is true for ion exchangers.
as proposed in Offenlegungsschrift no. 1,936,941. This method also requires regeneration in addition to further processing of the mercury-bearing regeneration liquid which also adds up to a high chemicals consumption rate.

For the reduction with hydrazine, the solution is mixed with that quantity of hydrazine which is necessary to reduce ionogenic mercury to the metallic form. The resulting emulsion is sent to a precoat filter where the mercury is retained; it has been found that the filtrate still contains 0.3 ppm mercury.

However, none of the known methods achieves complete elimination of the mercury from wastewaters. Residual mercury content is invariably in the order of magnitude of some tenths ppm.

Although the degree of mercury extraction so far achieved eliminates any acute risks of poisoning, the possible enrichment, for example in fish, does constitute a latent hazard. Because of the capacity of present-day industrial plants and the big volume of effluent wastewater discharged from these plants, even minute traces of mercury are hazardous to human health in view of the cumulative effect of enrichment. All endeavours that have so far been made were aimed at reducing the residual mercury content of wastewater to some tenths ppm. Nevertheless, despite substantial expenditures, a quantity of 30 g/day of mercury is discharged at a residual concentration of 0.3 ppm and an effluent wastewater flow rate of about 100 m$^3$/day.

A number of industrialized countries have issued stringent laws against mercury emissions into public waterways. An absolutely efficient process is needed to prevent
future compulsory shutdown of industries that depend on mercury.

The object of the present invention is to eliminate any emission of mercury by effluent wastewater and to reduce the expenditure involved as far as practicable.

According to the invention, the problem is solved by converting the pre-purified wastewater to flushing water through vacuum distillation and condensation, separating the blow-down from the vacuum distillation and returning the extracted brine into brine system. To achieve economical performance, hot brine from the electrolysis plant is used to serve as heat carrier for the vacuum distillation step. Part-condensation of the vapours from vacuum distillation is carried out with the aid of cold mercury-bearing wastewater.

The particular advantage achieved with the invention is that any emission of mercury by effluent wastewater is avoided because the wastewater is converted to flushing water for subsequent return to the process plant. The brine obtained from the blow-down is returned to the brine system of the plant.

Process industries are no longer menaced by the risk of compulsory shut-down. The processing of the residue from the vacuum distillation ensures a complete recovery of effluent-entrained mercury. No additional thermal energy is needed for vacuum distillation because hot brine is diverted from the alkaline chloride electrolysis plant, and its temperature is lowered to the level required for the electrolysis process. The cooling water required for condensing the vapours is no additional item because the transmission of heat by the brine means reduced need for
cooling the brine. The vacuum distillation unit may be fed with pre-purified wastewater having a higher content of residual mercury. Previous consumption figures of chemicals are substantially reduced in this way. The flushing water is circulated in a closed loop.

An example of application of the invention is illustrated in the accompanying drawing and is described in more detail below.

The mercury-bearing wastewater from an alkaline chloride electrolysis plant equipped with mercury cells is collected in wastewater pit 1. The wastewater contains finely distributed suspended metallic mercury and dissolved Hg in the form of Hg\(^+\), Hg\(^{++}\), (HgCl\(_2\))^\(\sim\), and (HgCl\(_4\))^\(\sim\) and is sent to mixing tank 3 by immersed pump 2. A conversion takes place after addition of hydrazine, and the mixture is then pumped by filter pump 4 to precoat filter 5. After this pre-purification, the filtrate still contains about 1.05 g/hour of mercury, the filtrate flow rate being 3.5 m\(^3\)/hour corresponding to a daily wastewater quantity of 80 m\(^3\). In addition, the wastewater which has a pH value of 12.5 also contains 0.22 ppm Fe(OH)\(_3\) in the form of Fe\(^{++}\), about 50 ppm organic and silicon compounds and 7 g/l of NaCl. This water passes at a temperature of about 25°C and atmospheric pressure into a receiver (not shown on the drawing) of rubber-lined steel which has a volume of 0.4 m\(^3\). From this receiver, the water is sent by a centrifugal pump through a pre-condenser 6 which serves for preheating the liquid from 25 °C to 45 °C to an evaporator 7. This evaporator is of the shell-and-tube type and is heated with brine which is at 78 °C and
has a concentration of 275 g/l of NaCl. The water in the evaporator is heated to 50 °C corresponding to a water vapour pressure of 92.5 Torr. The brine temperature drops to approximately 60 °C. For vaporizing the water, a vacuum of 92.5 mm Hg is applied which corresponds to the water temperature of 50 °C. This vacuum is produced by a motor-driven water seal pump of grey cast iron. The water vapour is withdrawn through pre-condenser 6 where part of the vapour condenses while the wastewater is pre-heated. This pre-condenser 6 is of the shell-and-tube type; it has a heat-exchange area of 7 m² and is equipped with tubes of metal alloy containing nickel and copper. The balance of the water vapour passes, together with the condensate, to main condenser 8 which is also of the metal alloy containing nickel and copper shell-and-tube type with tubes of similar size and which is tied-in to vacuum pump 9. This shell-and-tube type condenser has a heat-exchange area of 135 m².

The cooling fluid, viz. cooling water of 24 °C, passes across the tube side, and its temperature rises to 35 °C. The water vapour condenses completely while the condensate passes through a barometric leg at a temperature of 50 °C into receiver 10 from where it is fed back into a flushing water system of a centrifugal pump 11. This water is withdrawn for use from the flushing water system and returns as mercury-bearing wastewater to the wastewater pit referred to before. The flushing water may also be used for end box cleaning and for lean brine preparation.

The evaporation step referred to above leads to a concentration of impurities in the wastewater. In order to prevent crystallization of dissolved NaCl, which is the main constituent of the impurities, provision is made for an...
intermittent blow-down. A trap 12 which as a volume of 115 litres and which remains permanently filled with wastewater is mounted below evaporator 7.

As soon as the concentration of the wastewater has risen from 7 - 10 g/l of NaCl to 210 - 300 g/l of NaCl, a portion of 115 litres which corresponds to one thirtieth of the total volume of wastewater per hour must be drained. For this purpose, the trap is actuated through an adjustable timer, the time intervals being determined against density measurements. The drained brine passes to a receiver 13 which is sized to hold the daily volume of blow-down. This brine is sent through separator 14 into the brine system. Separator 14 is provided to retain Hg, Fe(OH)₃, sand, and other solid particles which are also concentrated in the evaporator. The mercury-bearing dry sludge is sent, together with the sludge from the precoat filter, to a mercury distillation oven where the mercury is recovered.

The above example describes the application of the invention in conjunction with an alkaline chloride electrolysis plant. It is evident that the invention permits of modifications in that, for example, the thermal energy for the wastewater and the cooling fluid for the flushing water may be diverted from economic sources other than the plant itself.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A process for the treatment of mercury-hearing waste-water from alkaline chloride electrolysis plant where mercury losses are encountered which are removed with the aid of flushing water, said wastewater having been subjected to pre-purification by means of chemical reduction and by filtration, the improvement which comprises converting the pre-purified wastewater to flushing water by means of vacuum distillation and condensation, separating the blow-down from the vacuum distillation and recycling the brine obtained into the brine system.

2. A process according to claim 1, which comprises using hot brine from the electrolysis plant for the vacuum distillation.

3. A process according to claim 1 or claim 2, which comprises performing part-condensation of the vapours from vacuum distillation by means of cold mercury-bearing waste-water.

4. A process for the treatment of mercury-beraing waste-water from an alkaline chloride electrolysis plant substantially as hereinbefore described with reference to the accompanying drawing.

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