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MEMORANDUM

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DATE: October 18, 1960

TO: R.W. Johnson

FROM: B.R. Bronfin, D.M. Jenkins, and E.E. Wright, Jr.

SUBJECT: Purification of Mercury Contaminated Lithium Hydroxide

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SUMMARY

The object of this investigation was to determine an economical method of preparing pure lithium hydroxide from a mercury-contaminated lithium hydroxide monohydrate salt presently produced as a waste product. Pure lithium hydroxide has application for chemical removal of carbon dioxide from air and general open market sale if the mercury contamination is reduced to approximately one part per billion.

Because of the uncertainty of the form of the mercury contaminant, different purification methods were explored on a laboratory scale which could be applied to the industrial waste stream.

The purities obtained from treatment of typical industrial waste samples (~6 ppm mercury, on a dry salt basis) for the four methods studied are shown in Table I.

Table I

Purification Obtained from Treatment of Industrial Waste Samples of Lithium Hydroxide Salt

Recrystallization	0.001 - 0.01 ppm
Sulfide treatment	0.01 - 0.1 ppm
Organic extraction of chelates	~2 ppm
Air heating	~6 ppm

The experimental results indicate that the predominant mercury contaminant existed as mercuric oxide, which was deposited in the by-product salt when the solubility of mercuric oxide, 60 ppm, was exceeded in aqueous lithium hydroxide solution.

To purify a fraction of the industrial by-product salt, a crystallization system, utilizing the difference in solubility of lithium hydroxide and mercuric oxide, is proposed. Total stream purification, using sulfide treatment, is expected to be less effective than recrystallization due to the difficulty in physical removal of the mercury contaminant, as mercuric sulfide, from solution.

INTRODUCTION

An available market exists for pure lithium hydroxide for general use in chemical processing. The demand in this market has been expanded by the application of lithium hydroxide for removal of carbon dioxide from closed air systems (e.g., in atomic submarines). Lithium hydroxide, having a high sorption per unit weight, appears as one of the best chemicals for removal of carbon dioxide; the reaction is:

$$2LiOH + CO_2(g) \longrightarrow Li_2CO_3 + H_2O \qquad 31.9 \text{ kcal/gmol } (\underline{10}) \qquad (1)$$

An available processed lithium hydroxide salt, $LiOH \cdot H_2O$, contains enough mercury, from six to ten parts per million by weight, to prohibit its application in many chemical processes and in closed human environments. If this salt, having a high mercury assay, is used for carbon dioxide sorption, enough toxic mercury vapors are introduced into the processed air to make it poisonous to the human system.

Large quantities of lithium hydroxide are being produced as a by-product at the present, and large additional supplies of processed salt are on hand.

The purpose of this investigation was to purify this contaminated salt to within established tolerance limits. A prime consumer, the U.S. Navy, has established an air tolerance limit in human environments at 0.01 mg Hg/ m^3 air, to be called the Navy Tolerance Limit, or NTL (19). Because of uncertainties in the nature of the contaminant in the processed salt, the Navy has placed a tolerance level on the solid of 0.5 parts per billion by weight (16). Since the average concentration in the processed salt is 6 ppm Hg, mercury concentration reduction by a factor of 12,000 must be achieved to meet this specification.

POSSIBLE TREATMENT METHODS

Since the form of the mercury contaminant occurring in the processed salts and solutions was unknown, different physical and chemical purification methods were attempted. The procedures of these methods were designed for scale-up application to the industrial waste stream.

Physical Treatment

Recrystallization. Extrapolation of the data of Seidell (14), shows that the equilibrium concentration of mercuric oxide in caustic solution would correspond to $\sim$60 ppm mercury in the liquid. This concentration is roughly the same as that present in the mother liquor of the industrial crystallizer. If the liquor above the recrystallized salt were never allowed to reach 60 ppm, the mercury could be maintained in solution and would not coprecipitate with the $LiOH \cdot H_2O$ crystals.

Air Heating. When the hydroxide is heated by the heat of reaction (Equation 1), some release of mercury vapor has been observed (1). Physical treatment of the contaminated hydroxide with a stream of hot, CO_2-free air could wash the salt and make it inactive to further release of mercury by heat generated in the carbon dioxide absorption reaction.

Chemical Treatment

Chelation. Chemical treatment could complex the mercury in chelate forms that hold the mercury in solution during the formation of pure lithium hydroxide monohydrate crystals. The chelating agents, ethylenediaminetetracetic acid (EDTA) (3), mercaptoacetic acid (17), and cysteine (16), could affect increased contaminant solubility. This method could be used with fractional crystallization to improve the purity.

Sulfide Treatment. Another economical chemical treatment is the addition of sulfide to form mercuric sulfide. The reaction is:

$$Hg^{++} + S^{=} \longrightarrow HgS \downarrow , \quad K \approx 10^{+49} \quad (\underline{10}) \qquad (2)$$

The mercuric sulfide formed could be filtered from the aqueous lithium hydroxide solution before crystallization. This method would leave metallic mercury in solution and would require removal by one of the above methods, or precipitation with elemental sulfur.

Elemental Sulfur Treatment. Metallic mercury could be removed by passing the lithium hydroxide solution through a sulfur bed, resulting in the formation of the insoluble mercuric sulfide

$$Hg^{o} + S_2^{o} \longrightarrow HgS \downarrow , \quad K \approx 10^{37} \quad (\underline{10}) \qquad (3)$$

which would be trapped in the fine sulfur bed.

A series of experiments was performed to investigate the possibilities of these treatment methods.

PROCEDURE

This investigation considered four methods to purify lithium hydroxide: recrystallization, sulfide-sulfur treatment, chelation, and air heating.

Recrystallization

Two methods of recrystallization were investigated. In the first method a nearly saturated solution of lithium hydroxide, containing about 10 ppm mercury, was vacuum evaporated to one-third volume and cooled to room temperature with approximately 50% $LiOH \cdot H_2O$ recovery. In the second method, acetone was added to the lithium hydroxide solution (1:5), precipitating approximately 20% of the lithium hydroxide, as the monohydrate, $LiOH \cdot H_2O$.

Sulfide-Sulfur Treatment

In the sulfide treatment excess sodium sulfide was added to the lithium hydroxide solution and the solution filtered to remove mercuric sulfide. Nickelous sulfate or ferric nitrate was then added to remove excess sulfide. The treated lithium hydroxide (aq.) was again filtered, passed through a sulfur bed, and vacuum evaporated to dampness.

Chelation

An excess of each of the three chelation agents, ethylenediaminetetracetic acid (EDTA), mercaptoacetic acid, and cysteine, was added to a nearly saturated lithium hydroxide solution containing $\sim$ 55 ppm mercury. The EDTA treated solution was vacuum evaporated to 40% volume, centrifuged, washed, and dried. Since mercapto-agents were observed to decompose during the heating in the vacuum evaporation step, lithium hydroxide monohydrate was precipitated from the chelate solutions with acetone, as described in the recrystallization procedure.

Air Heating

In the air heating technique carbon dioxide free air was heated to 200°C and passed through lithium hydroxide monohydrate salt, containing 2 ppm mercury, in a fluidized column.

Analysis

Samples from all treatment runs were heated at 220°C to form the dehydrated salt from the lithium hydroxide monohydrate, which is the specie crystallized from aqueous solution. Assays were then made upon the calcined salt by a sensitive gold-amalgam test.

RESULTS

Mercury concentrations in the purified lithium hydroxide salt are given in Table II for the four purification methods investigated: recrystallization, sulfide treatment, chelation, and air heating. These concentrations were determined from a gold-amalgam analysis. Mercury concentrations in air that had been passed through the treated salt samples were determined by an ultraviolet absorption test.

Table II

Mercury Concentrations of Samples Prior to and after Various Treatments

Procedure	Starting Material	Starting Concentration Hg(ppm)	Assay After Treatment Hg(ppm)	Air Concentration (mg/m^3)	(% NTL)
Average salt, $LiOH \cdot H_2O$	-	3	-	0.080	800
Recrystallization, from acetone-water solution					
- first	$LiOH \cdot H_2O$, salt	3	.100	-	-
- second	"	.100	.001-.$\underline{010}$	-	-
- third	"	.01	.$\underline{001}$-.01	0.024	240
Recrystallization, by evaporation, from aqueous solution					
- first	$LiOH \cdot H_2O$, salt	3	.$\underline{001}$-.01	-	-
- second	"	.001	.$\underline{001}$-.01	-	-
- third	"	.001	.1	0.004	40
$S^=$ and S^o Treatment,					
- 25°C	LiOH solution	12	.1	-	-
- 90°C	"	11	.$\underline{01}$-.1	0.008	80
Chelation,					
- mercaptoacetic acid	LiOH solution	55	~ 2	-	-
- cysteine	"	55	~ 2	-	-
- ethylenediaminetetracetic acid	"	55	~ 2	-	-
Air Heating (200°C)	$LiOH \cdot H_2O$, salt	3	~ 2	-	-

Underlined values indicate concentration closest to actual value as indicated by assay.

DISCUSSION OF RESULTS

The possible forms of the mercury in the saturated caustic solution of lithium hydroxide are: mercuric oxide (HgO), metallic mercury (Hg^o), mercuric ion (Hg^{++}), and dimercurous ion (Hg_2^{++}).

Existence of HgO in Solution

No lithium hydroxide solution had a mercury concentration exceeding 60 parts per million (ppm). Seidell has reported the solubility of mercuric oxide in caustic solutions as follows (14):

Caustic	Temperature	Solubility	
.45 M LiOH	25°C	0.0025 M	50 ppm
4 M NaOH	25°C	0.003 M	60 ppm

The saturation levels of the processed lithium hydroxide solutions therefore correspond to the solubility limit of mercuric oxide at similar conditions and suggest the predominance of mercuric oxide. From the purifications obtained in the recrystallization method it is postulated that more than 99.99% of the mercury present in processed lithium hydroxide salt or solution exists in the mercuric oxide form.

Existence of Other Mercury Species

The concentration of metallic mercury in the processed lithium hydroxide solution or salt would be small as shown by the data of Seidell for the solubility of mercury in aqueous solution (14):

$$\text{solubility limit} = 0.02 - 0.03\ \mu gm/l$$

Mercuric and mercurous ion concentrations in this caustic solution would be negligible, these species being converted to the mercuric oxide by the reactions:

$$Hg^{++} + 2OH^- \longrightarrow HgO + H_2O \qquad K = 4.6 \times 10^{22}\ (10)$$

$$\tfrac{1}{2}Hg_2^{++} + 2OH^- \longrightarrow Hg_2O + H_2O \qquad K = 3.6 \times 10^{25}\ (10)$$

$$Hg_2O \longrightarrow HgO + Hg^o$$

Behavior of Mercuric Oxide in Recrystallization

The degree of purification obtained by the recrystallization procedure resulted from dissolving the salt (typically 6 ppm mercury) in an excess of water to form a solution well below mercuric oxide saturation. Further recrystallization could not produce significant reductions beyond the limit predicted by solubility already attained in the first stage. In these solutions other species, such as metallic mercury, may begin to predominate.

The reduction of mercury contamination, from 6 ppm to <0.01 ppm, in two separate experiments indicated that purification by a factor of about 10^3 can be attained through recrystallization.

The purification obtained with recrystallization had been previously demonstrated, although to a lesser degree, with this mercury-lithium hydroxide system on both laboratory and industrial scale (1). However, in these investigations, which reported $>$ 0.1 ppm mercury in salt, complete studies with multiple stage crystallization and experimental replications were not made.

Mercuric Oxide Reaction with Sulfide

Sulfide treatment of the lithium hydroxide solutions, followed by the contacting of the solution with elemental sulfur, produced reasonably high degrees of purity. The formation of black mercuric sulfide particles was observed as the sulfide was added and given time to undergo reaction. As the treated solution was drawn through the elemental sulfur bed, black discoloration appeared in the upper portion of the bed.

Purification is obtained by the sulfide reacting with the mercuric oxide species to form the black insoluble mercuric sulfide (HgS solubility = 10^{-44} ppm Hg; HgO solubility = 60 ppm Hg):

$$HgO + S^{=} \longrightarrow HgS\downarrow + 2OH^{-} \qquad K = 10^{26} \qquad (\underline{10})$$

Because of the large equilibrium constant for the above reaction, much higher degrees of purity would be expected. Two factors could contribute to the residual mercury contamination observed:

1) Entrainment of colloidal and sub-colloidal mercuric sulfide particles in the filtrate which could not be separated by the simple filtration used in the experimental procedure. When the filtrate was evaporated to dampness (See Appendix A-2), the small amounts of mercuric sulfide passed by the filter deposited on the lithium hydroxide salt causing the observed contamination. Better results would be expected if the salt were not evaporated to dampness, but to a slurry, with mercuric sulfide retained in suspension. However, this procedure would introduce the effect of a partial recrystallization and obscure the effect of sulfide treatment. Also, coprecipitation (8) of residual mercuric sulfide with the lithium hydroxide salting out of solution could increase the contamination above that predicted by recrystallization.

2) The reaction rate in trace concentration of contaminant (HgO) and reactant ($S^=$) may be controlled by diffusion and be much slower than in high concentrations. The gradual change in coloration from the dull yellow sulfide ion to the dull black dispersed metal sulfides which were observed during the 60 minute stirring time suggest slow rate process. A slow rate process may also be involved in the dissociation of the mercuric oxide to mercuric ions which act as intermediates in the formation of the insoluble mercuric sulfide.

Effect of Temperature

A repeat of the sulfide-sulfur treatment was made with the solution at 90°C and resulted in only a slightly greater purification. The lack of significant change in the purity indicates that the over-all activation energy, for the mercuric oxide decomposition, aqueous diffusion, and mercuric sulfide formation, is large enough not to be affected by a 60°C change in temperature. It is believed that the reaction has already closely approached equilibrium at both temperatures within the allowed reaction time, and therefore entrainment is the remaining cause of observed salt contamination.

Action of the Sulfur Bed

The expected redox reaction between sulfur and metallic mercury exhibits a favorable equilibrium constant:

$$Hg^o(l) + S^o(s) \longrightarrow HgS(s) \qquad K \approx 10^8 \quad (\underline{10})$$

Since the removal involves a liquid solid reaction, experimental contact areas, surface conditions, and concentrations may have had an adverse affect upon the reaction rate. The evaluation of the efficiency of the sulfur column in removing metallic mercury by oxidation to mercuric sulfide, is further complicated by the collection of mercuric sulfide carried into the bed by the filtrate stream.

Removal of Reagents

After the filtration step excess sulfide from the treated solutions was quantitatively removed with an excess of other metal ions. Tests of typical sulfide treatment runs yielded less than 10^{-4} $\underline{M}$ $S^=$, the lower limit of the nitroprusside spot test (6). Sulfur particles, however, were entrained in the treated solution from the sulfur column, but were dissipated at the drying temperatures.

Previous Work with Sulfides

Previous work with this system in the laboratory indicated purities in the range of 1 ppm mercury could be obtained with sulfide treatment (1). An industrial sulfide treatment, which provided a holdup tank for reaction time, produced salts in the 1 ppm range, but equipment failures prohibited the establishment of a steady-state mercury concentration in the salt (1).

This previous work should be analyzed carefully to observe the extent to which the effects of recrystallization, entrainment, and reaction time have been considered. A redesign of the experimentation considering these effects could bring the results of the previous investigation up to or beyond the levels of purity observed here.

Behavior of Mercuric Oxide in Presence of Chelating Agents

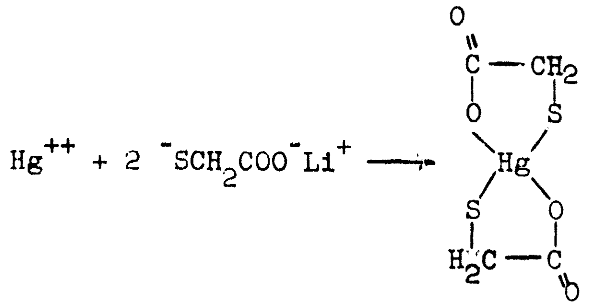
Neither mercapto- nor carboxyamino-chelating agents reduced the mercury contamination in the lithium hydroxide appreciably. Salts of only ~2 ppm purity were produced from lithium hydroxide solutions of original concentration of 55 ppm to which chelating agents were added.

A similar failure of chelation agents to produce substantial degrees of purification has been noted both in laboratory and industrial experiments (1). The mercapto- chelation agents had not been previously investigated in the Li-OH-HgO system, however.

Mercapto-Chelating Agents

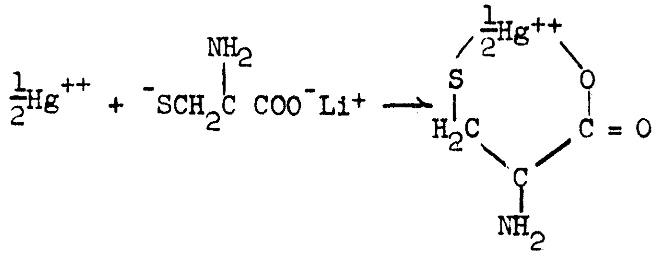
Initial trials using the mercapto-chelating agents, mercaptoacetic acid and cysteine, appeared to be effective. The strong mercury-sulfur bond exhibited in the insoluble mercuric sulfide compound is illustrated in the association constants for these organic chelation agents:

$Hg^{++} + S^{=} \longrightarrow HgS$ $K = 10^{49}$ (10)



$Hg^{++} + 2\ {}^{-}SCH_2COO^{-}Li^{+} \longrightarrow$

$K = 10^{44}$, pH=14 (17)



$\frac{1}{2}Hg^{++} + {}^{-}SCH_2C(NH_2)\ COO^{-}Li^{+} \longrightarrow$

$K = 10^{44}$, pH=14 (16)

However, the attempts to extract the mercuric complexes which were formed into organic layers (ethyl ether, acetone) failed to free the aqueous layer of mercury contamination. The salt contamination is created because mercury complexes remaining in the aqueous layer are placed on the salt when the aqueous solution is heated to dryness.

Carboxyamino-Chelating Agents

Since the association constant of the carboxyamino-chelating agent, ethylenediaminetetracetic acid, is smaller than the mercapto-chelating agents and of the same order of magnitude as the association constant of mercuric oxide, this chelation would be expected to be less effective:

$$Hg^{++} + 2OH^{-} \longrightarrow HgO + H_2O \qquad K = 5 \times 10^{22} \qquad (\underline{10})$$

$$Hg^{++} + EDTA \longrightarrow Hg^{++}(EDTA) \qquad K = 10^{22} \qquad (\underline{3})$$

The repetition of the results using this chelation agent suggests that the phenomenon of the deposition of mercury, in a chelate form, on the lithium hydroxide salt is occurring in some stage of the drying procedure required in the laboratory experiment.

Mercuric Oxide Stability in Air Heating

The treatment of a column of lithium hydroxide monohydrate with a fluidizing carbon dioxide-free air blast at 200°C contributed little to the reduction of the mercury concentration in the salt. Starting with a salt containing 6 ppm mercury (based on weight of dehydrated lithium hydroxide), treatment at this temperature for 30 minutes of fluidization resulted in a product of over ~2 ppm mercury (on the same basis).

In the hot gas treatment the mercury contained in processed lithium hydroxide salt is not sufficiently volatile to be quantitatively driven off at 200°C, nor can it be totally decomposed into a volatile state. A comparison of vapor pressures at 200°C demonstrates that this treatment would not be effective for mercuric oxide, while free mercury would be noticeably reduced:

p_{HgO} is negligible

$p_{Hg^{o}}$ = 17.3 mm at 200°C ($\underline{13}$)

$$\text{HgO decomposition temperature at 1 atm} = \begin{cases} 544^{\circ}C & (\underline{12}) \\ 425\text{-}490^{\circ}C & (\underline{5}) \end{cases}$$

RELIABILITY OF CONCENTRATION DETERMINATIONS

Solid Salt Concentrations

A gold amalgam analysis was made upon the lithium hydroxide salt samples to determine residual mercury contamination. The bracketed values reported in the data show high confidence limits in the range for which this determination is valid, that is 0.01 to 500 part-per-billion (ppb) mercury.

Air Concentrations

The determination of mercury vapor contamination in a controlled air stream passed through the lithium hydroxide salt sample was made by measurement of ultraviolet absorption at the 2357Å Hg I line. However, determination made by this technique did not correlate with the solid salt determinations as shown in Table III.

Table III

Condensation of Experimental Data Showing Runs for Which Both Salt and Air Concentrations Were Determined

	Salt Concentration (ppm)	Air Concentration (mg/m^3)
Organic Recrystallization	0.001 - 0.01	0.024
Evaporative Recrystallization	0.001 - 0.01	0.004
Sulfide Treatment	0.01 - 0.1	0.008

A possible explanation of this behavior is the adsorption of particles of salt or condensation collecting within the UV absorption cell in the vapor detection apparatus (Appendix B-3).

CONCLUSIONS

1) Purification of processed lithium hydroxide monohydrate salt by recrystallization can achieve mercury concentrations in the range of one to ten parts-per-billion.

2) Mercapto- chelation agents may assist in the recrystallization process by increasing the effective solubility of mercury species in the solution from which the crystals are to be formed.

3) Purification by the addition of sulfide to form insoluble mercuric sulfide can achieve mercury concentrations in the treated salt in the range of ten to one hundred parts-per-billion, provided precautions are taken to fully remove the insoluble sulfide.

4) The mercury species which is predominant in the processed lithium hydroxide salts and solutions is indicated to be mercuric oxide, and its solubility determines the mercury concentrations in the product salt.

RECOMMENDATIONS

Recommendations for future work are:

1) Quantitative evaluation of the effect of chelation agents in increasing the solubility of mercury species in caustic solution.

2) Thorough study of the purification possible in successive recrystallizations, giving particular attention to elimination of trace impurities accumulated in laboratory ware and reagents.

3) Separate evaluation of the effect of the elemental sulfur bed, giving attention to the fineness of the sulfur particles used and their effect as a filter medium.

4) Examination of a gas heating process using a non-reactive gas (e.g., nitrogen) at temperatures near the decomposition level of mercuric oxide.

5) Examination, by refined micro-techniques, of the size and properties of the mercuric sulfide formed at trace concentrations.

6) Recalibration of the vapor test apparatus to determine the effect of entrained water or salt fines, and the range of concentrations for which it is reliable.

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APPENDIX

A. Experimental Procedure

The following outlines the experimental methods used to reduce mercury contamination in processed lithium hydroxide.

1. Recrystallization

a. By Evaporation. In 15 liters of distilled water, 3000 grams of $LiOH\cdot H_2O$ containing 2 ppm Hg was dissolved. The solution was evaporated under vacuum at approximately 50°C to 1/3 volume and then cooled to 25°C. $LiOH\cdot H_2O$ was separated by filtration and washed with a 1:1 water-acetone mixture. About 50% $LiOH\cdot H_2O$ was recovered. This procedure was repeated using 1300 grams $LiOH\cdot H_2O$ from the first recrystallization in 6 liters of distilled water and 650 grams from the second recrystallization in 3 liters of distilled water, respectively.

b. By Acetone Precipitation. In 6 liters of distilled water 1150 grams of $LiOH\cdot H_2O$ containing 2 ppm Hg was dissolved and 1050 ml of acetone added. $LiOH\cdot H_2O$ crystals were collected on a filter and washed with 1:1 acetone-water mixture. This procedure was repeated using 140 grams $LiOH\cdot H_2O$ from the first recrystallization in 600 ml water and precipitating with 120 ml acetone. These two recrystallizations were analyzed for Hg. Since there was not enough LiOH for a third recrystallization, another series of recrystallizations was made using 2400 grams $LiOH\cdot H_2O$ (2 ppm Hg) in 12 liters of water. The 250 grams of $LiOH\cdot H_2O$ obtained from the first recrystallization was dissolved in one liter of water and the 50 grams of $LiOH\cdot H_2O$ obtained from the second recrystallization in 150 ml of water. The volume of acetone was 20% that of the water. The yield of the third recrystallization was 4 grams of $LiOH\cdot H_2O$ which was analyzed for Hg by the gold amalgam method.

2. Sulfide reatment

To 1000 ml 4.5 M LiOH solution containing 11-12 ppm Hg, 5 ml 0.0087 M Na_2S solution was added to give fifteen times the stoichiometric amount for the formation of HgS. The solution was then mixed for thirty minutes and filtered. A twofold excess of either 0.0174 M $NiSO_4$ or 0.017 M $Fe(NO_3)_3$ was added to remove unreacted sulfide. The solution was mixed for thirty minutes and filtered. The solution was then passed through an 8 cm long bed of sulfur flowers at about 2 $cm^3/sec\text{-}cm^2$ column cross section. Finally the solution was vacuum evaporated to dampness.

3. Chelation

The amounts of the three chelation agents, mercaptoacetic acid, cysteine hydrochloride and ethylenediaminetetracetic acid (EDTA) added to 4.5 M LiOH containing 55 ppm Hg are shown in Table IV. The mixtures were stirred for 30 minutes. When EDTA was used, the solution was vacuum evaporated to 40% of the original volume. The slurry was centrifuged and the solid was collected, washed with acetone, and dried. Mercaptoacetic acid and cysteine decompose at high temperatures. When these agents were used, $LiOH \cdot H_2O$ was precipitated by adding 1 volume of acetone for each 4 volumes of solution. The $LiOH \cdot H_2O$ was then recovered by filtration, washed with 1:1 acetone water mixture and dried.

Table IV

Amounts of Chelation Agent Addition

Agent	Amount 4.5 M LiOH Solution (liters)	Amount Agent (moles)
Mercaptoacetic acid	1.5	0.0144
Cysteine	1.0	0.01
EDTA	1.5	0.015

4. Air Heating

Air was passed through a saturated LiOH solution to remove CO_2 and then heated to 200°C in a tube furnace. The hot air was passed through a 24" column of $LiOH \cdot H_2O$ containing 2 ppm Hg. The column was also gently heated with a Bunsen burner to hasten the decomposition of the monohydrate. After the water of crystallization had been driven off, the column was operated as a fluidized bed for 45 minutes. The bed contained about 100 grams of LiOH.

B. Analysis of Mercury in LiOH

1. Gold Amalgam Method (15)

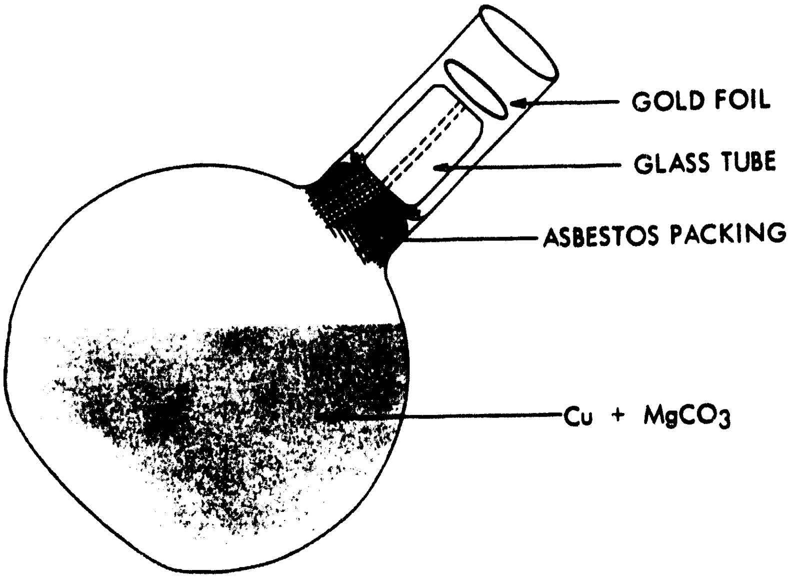
This method is valid only for Hg concentrations between 0.00001 and 0.5 ppm. A ten gram sample is dissolved in distilled water, diluted to 500 ml, and neutralized with aqua regia. A 5 ml excess of acid is added. Pure copper dust (2.5 grams) is added, stirred for 60 minutes, and left to settle for two hours. Both supernatant liquid and filtrate are filtered separately. The filtrate is washed with 50 ml absolute methanol, 25 ml ethyl ether, and then air dried for 45 to 60 minutes or until the ether odor has disappeared. After dessicating overnight, the copper dust is placed into a 5 ml flask and 0.05 grams $MgCO_3$ added. In the flask neck are added a pinch of asbestos, then a glass tube, and finally a gold foil disc (See Figure 1a). The flask neck is wrapped with wet filter paper and heated gently in a gas flame until cherry red. The gold foil is then removed and compared under low power microscope with standard samples of 0.1, 0.01, 0.001, 0.0001, and 0.00001 ppm Hg. This method is only good to within a factor of 10.

2. Spot Test (15)

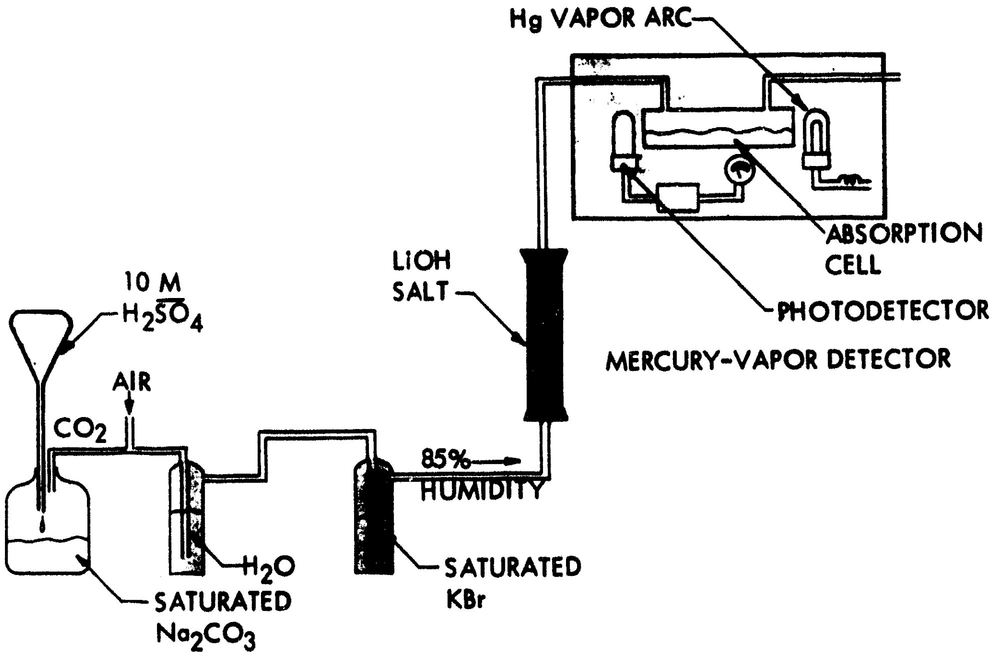
This method is good for 10 ppm Hg or greater. An indicator reagent is prepared by dissolving one gram diphenylcarbazone in 100 ml 95% ethyl alcohol. To a 50 ml sample, 20 ml of concentrated HNO_3 is added and the solution evaporated to 1 to 2 ml. This is diluted to 50 ml with distilled water. Five drops of this solution are placed on a spot plate and the pH adjusted to 3.5-4.0 with 0.1 or 0.01 M HNO_3 or LiOH. The solution is diluted to ten drops with distilled water. Ten drops of a standard solution are placed in adjacent depressions in the spot plate. One drop of indicator is added to each solution and the resulting color compared to the standards.

3. Vapor Test (1)

The apparatus for the vapor test is shown in Figure 1b. Carbon dioxide is generated by adding 10 M H_2SO_4 to a saturated Na_2CO_3 solution at the rate of 0.1 cc/sec. The CO_2 is mixed with an air stream, providing 500 cc/min/cm^2 of LiOH tube cross-section, at 20% CO_2. The gas mixture is bubbled through water, saturated KBr solution to produce a standard 85% humidity, and then passed through a 3 cm diameter tube filled to a depth of 15 cm (approximately 60 grams of LiOH). The gas stream from the bed is then passed through a G.E. Vapor Detector (20), sensitive to absorption at the 2357Å Hg I line, to obtain a reading (after a 5 minute stabilization interval) calibrated in mercury concentration units.



A. GOLD AMALGAM ANALYSIS FLASK



B. AIR TEST APPARATUS

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
ENGINEERING PRACTICE SCHOOL
UNION CARBIDE NUCLEAR COMPANY
Division of Union Carbide Corporation

Figure 1

A. Gold Amalgam Analysis Flask
B. Air Test Apparatus

DATE	DRAWN BY	FILE NO.	FIG.
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C. Industrial Systems to Produce Uncontaminated Lithium Hydroxide

Figure 2 is a schematic diagram of a present recrystallization installation producing impure salt.

Analysis of the experimental laboratory results indicated that salt contamination is due to the mother liquor of the crystallized $LiOH \cdot H_2O$ being saturated with HgO. At startup it is probable that the recycled slurry from the crystallizer and mother liquor from the centrifuge contain approximately 12 ppm Hg (weight mercury to weight salt). However, because more HgO is coming into the system than is leaving, the slurry and mother liquor streams become more saturated in HgO, until its solubility limit, 0.003 $\underline{M}$ is reached. This corresponds to a mercury concentration of 60 ppm Hg (weight Hg to weight solution). Thereafter equilibrium requires that a mercury material balance on entrance solution and exit salt will be met, or that the mercury contamination of the exit salt will be approximately 6 ppm Hg (weight Hg to weight dry salt).

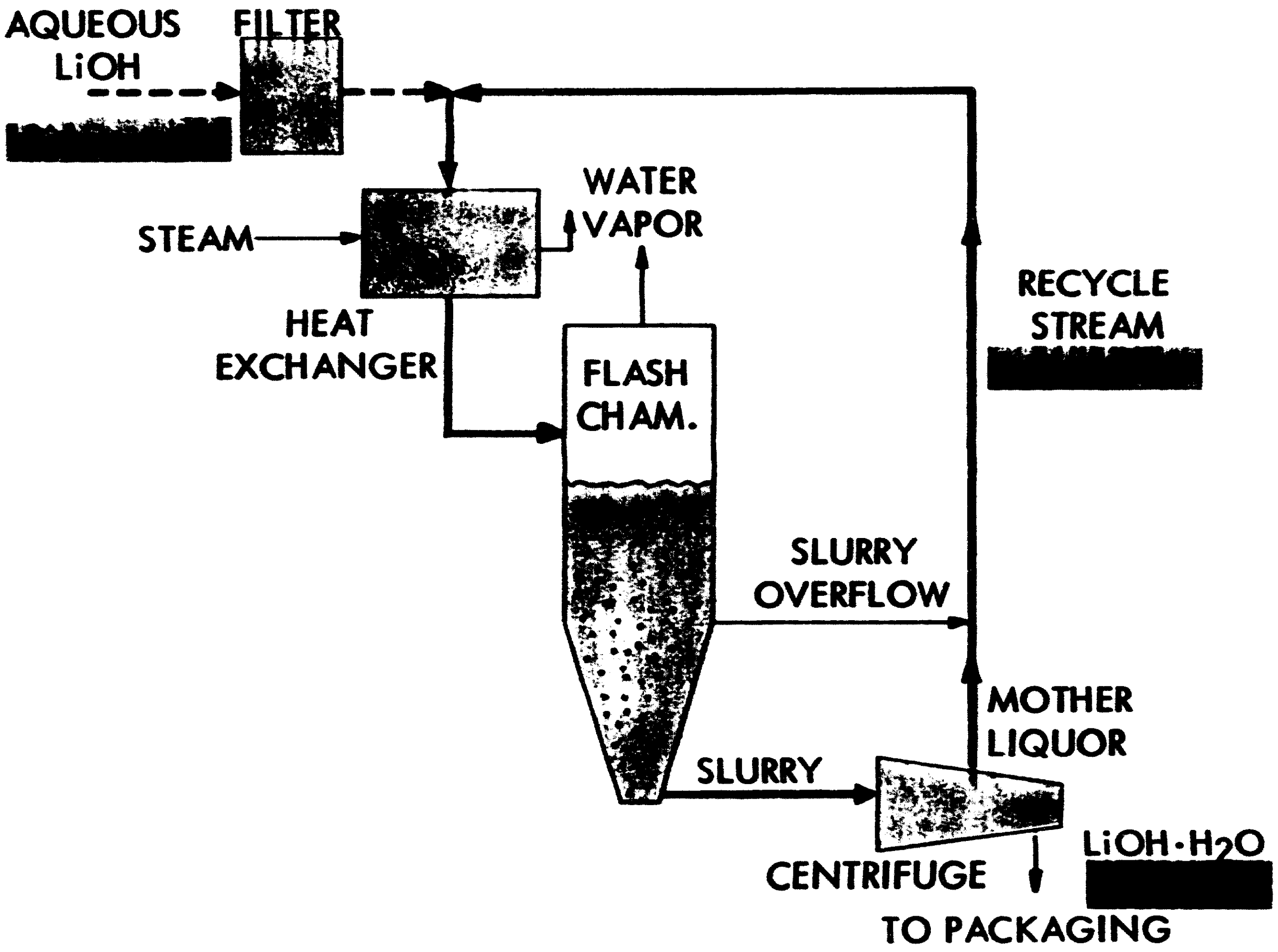
1. Parallel and Secondary Recrystallization

An industrial purification system, shown in Figure 3, would use parallel crystallization. A fraction of the feed solution after filtration is heated, flash crystallized and centrifuged in a secondary system, the slurry overflow and mother liquor being circulated to the primary impure stream. If partial crystallization in the secondary system is controlled such that the mother liquor never becomes saturated in HgO, salt leaving this section should contain only trace amounts of mercury, 1-10 ppb, as predicted by laboratory data. Using this method, no extra evaporation would be necessary if irreversibilities in the flash chamber are neglected. Additional cost would mainly involve amortization of the capital expenditure and maintenance costs for the secondary centrifuge, heat exchanger, and flash crystallizer.

As can be seen from Figure 3, the amount of feed directed to the parallel system may be varied according to the purified salt demand. The ratio of the flow in this stream to the total feed to the process may be varied from 0.0, at no demand, to 1.0 at high demand. In the latter case, the system will not be parallel to the impure system, but will be in series with it; that is, the total discharge from the pure system is feed to the impure system.

If sufficient purity is not obtained by the above method, a second recrystallization would be carried out on the semi-pure salt from the secondary unit. This would require another crystallizer and centrifuge unit, and the evaporation of the water used to redissolve the semi-pure salt. A schematic of this latter system is shown in Figure 4.

Because a large amount of salt containing ~6 ppm Hg is on hand, provision is made to purify lithium hydroxide salt supplies in the process which required two recrystallizations and additional evaporation.



EXISTING SYSTEM

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Figure 2

Existing System

DATE	DRAWN BY	FILE NO.	FIG.
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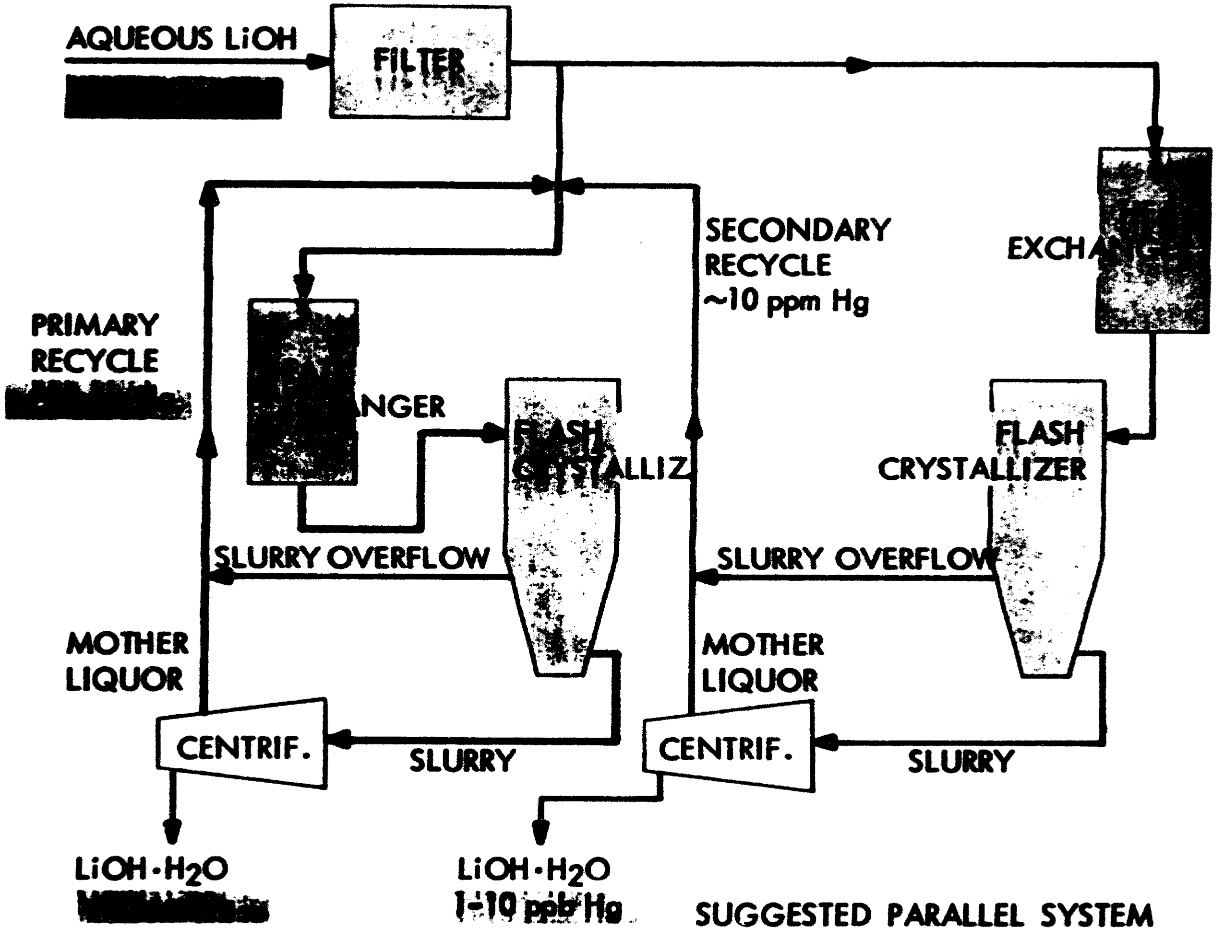

SUGGESTED PARALLEL SYSTEM

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Figure 3

Suggested Parallel System

DATE	DRAWN BY	FILE NO.	FIG.
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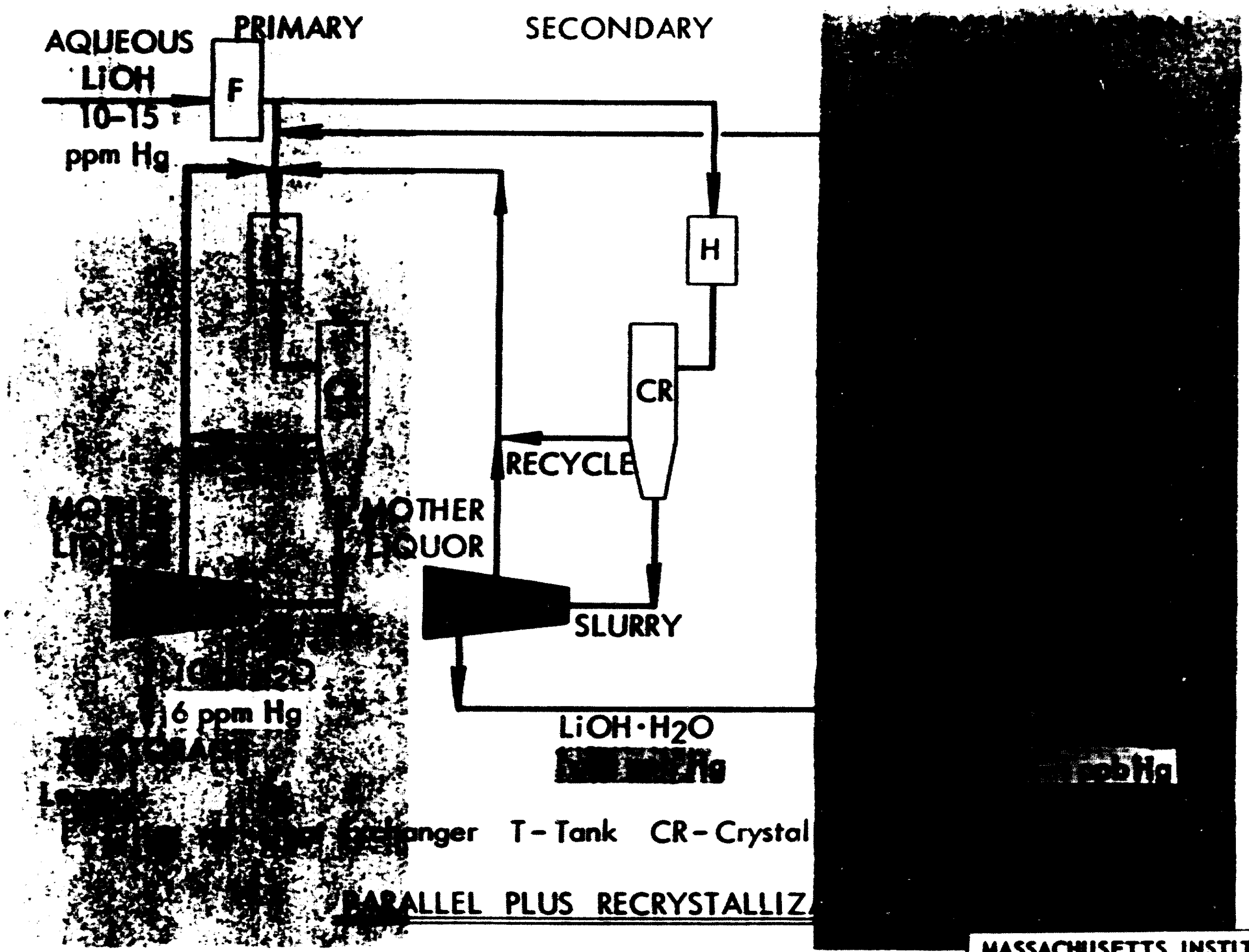

...anger T - Tank CR - Crystal [redacted]

PARALLEL PLUS RECRYSTALLIZ [redacted]

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Figure 4

Parallel Plus Recrystallization

DATE	DRAWN BY	FILE NO.	FIG.
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Since the entering feed is predominantly 12 ppm Hg, optimum evaporation would reduce the aqueous feed volume by one-fifth, to the saturation level of HgO, i.e., 60 ppm. More conservative reduction, e.g., one fourth, would be recommended for actual plant operation.

Laboratory work, using between one-third and one-fourth aqueous volume reductions cooled to 25°C, achieved approximately 50% salt recovery, which would certainly be adequate for partial stream purification. (Salt not recovered is recycled as mother liquor for recovery in the main, impure treatment stream, cf. Figure 3).

As mentioned below, chelation may allow greater volume reduction ratios, and consequently, greater salt recovery in the pure treatment stream.

2. Chemical Treatment

a. Sulfide. If purification of the total waste salt production becomes necessary, the use of a sulfide to precipitate mercury contaminant is recommended. The sulfide would be added to a stirred holdup tank upstream from the filter. The precipitated HgS would then be trapped on the filter, reducing the mercury concentration in the feed to between 10 and 100 ppb, based on the laboratory results of this investigation. The low cost of this treatment favors its use in conjunction with the crystallization methods discussed above.

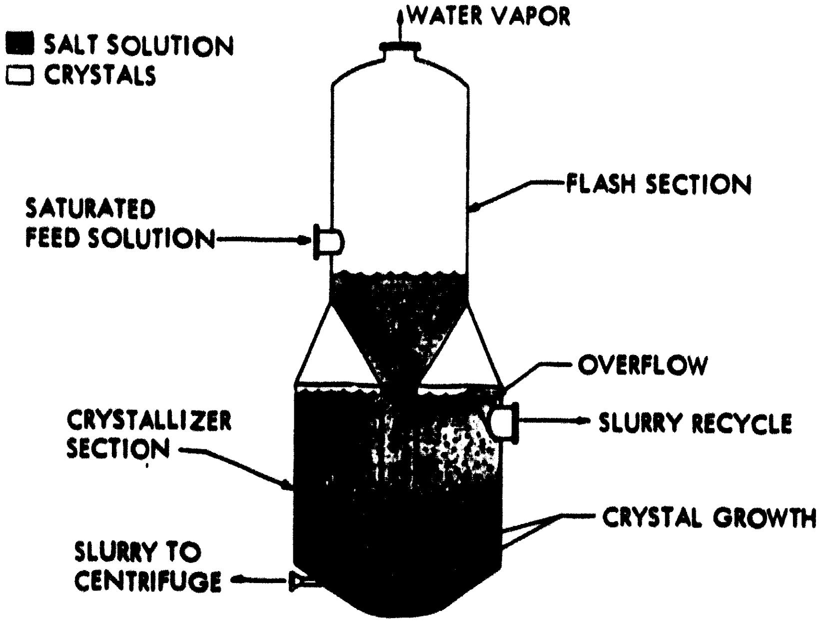
b. Chelation. Although chelation agents aided the separation by only a factor of 10 or less, they could be used in the recrystallization steps to increase the effective solubility of the mercury in the aqueous solution from which the $LiOH \cdot H_2O$ is formed.

3. Examination of Industrial Units

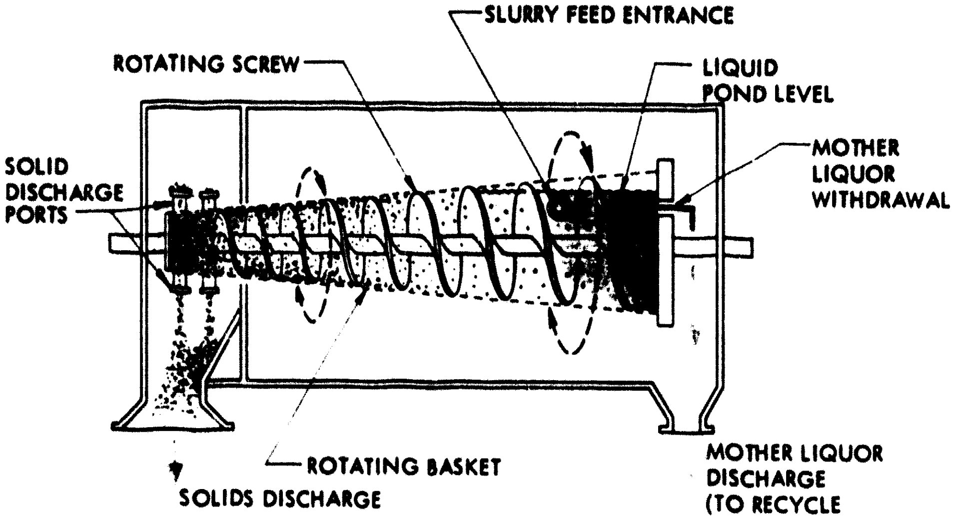
Consideration must be given to the capability of industrial equipment to achieve the same results as the laboratory techniques. The suggested purification process can utilize existing pieces of equipment and additional units of the same type. The following discussion examines these specific commercial units:

<u>Filter</u>. A standard filter press (utilizing National Filter Media 37 x 29 cloth and Eaton-Dikeman No. 953 filter paper) closely parallels laboratory filtration. This filter would be adequate for preliminary filtration as now employed; however, in trapping mercuric sulfide a more refined filtration technique is indicated from the failure of total laboratory filtration.

<u>Flash Crystallizer</u>. The Oslo evaporative type crystallizer (<u>4</u>), manufactured from a standard Struthers-Wells design, is shown in Figure 5a. The slow crystal growth promoted in gradual upward flow in the crystallizer



A. FLASH CRYSTALLIZER



B. CONTINUOUS CENTRIFUGE

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Figure 5

A. Flash Crystallizer
B. Continuous Centrifuge

DATE	DRAWN BY	FILE NO.	FIG.
10-18-60	GB & FC	EPS-Y-459	5

section maintains the crystals formed in suspension. This intimate crystal-solution association incorporated in the analogous laboratory crystallization procedure is favorable for pure crystal formation.

Continuous Centrifuge. The screw-drive continuous conical centrifuge (4), manufactured from standard design by Bird Filter Company (2), is shown in Figure 5b. In this unit the solids are discharged dry in isolation from the mother liquor withdrawal. This separation of mother liquor from salt can be expected to effect higher purity than the laboratory procedure of collecting salt on a filter and withdrawing the associated mother liquor through the salt cake.

D. Acknowledgements

The authors wish to acknowledge the assistance of L.S. Skeel and G.A. Burton, Jr. of the Alpha-4 Process Control Laboratory in analyzing the LiOH for Hg and E.E. Greeley of the Y-12 Glass Shop in the preparation of specialized glass apparatus.

E. Location of Original Data

The original data for this investigation conducted October 3-17, 1960, are located in unclassified data book No. 26 on file at the M.I.T. Engineering Practice School, ORGDP, Union Carbide Nuclear Company, Oak Ridge, Tennessee.

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