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LABORATORY RECORDS

ALLOY DEVELOPMENT PROJECT

STATUS REPORT:

INV 70

OREX PROCESS

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ALLOY DEVELOPMENT PROJECT

STATUS REPORT: OREX PROCESS

H. M. McLeod, Jr., Pilot Plant Supervisor

June 27, 1952

MATERIALS CHEMISTRY DIVISION

G. H. Clewett, Division Director

[redacted]

Edited by K. O. Johnsson

OAK RIDGE NATIONAL LABORATORY
Operated by
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION

Oak Ridge, Tennessee

Contract No. W-7405-eng-26

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PREFACE

With the prospect of an accelerated Orex program in fiscal 1953 and the addition of new personnel requiring orientation, this status report has been prepared for addition to the present reading file.

The report summarizes the results of the laboratory and initial pilot plant work carried out during the period between September 24, 1951, and June 1, 1952.

The material was prepared with the assistance of the following members of the Materials Chemistry Division: G. M. Begun, J. S. Drury, H. H. Garretson, D. A. Lee, A. A. Palko, J. W. Ramsey, A. C. Rutenberg, and A. D. Ryon.

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STATUS REPORT: OREX PROCESS

TEMPERATURE DEPENDANCY OF α

Using methods described elsewhere[1,2], single stage and multistage batch runs were performed to determine the temperature dependance of the single stage separation factor from 26°C to 99°C. These values are listed in Table I.

Table I

Laboratory Determinations of α

Temp°C	α	Uncertainty in α at 95% Confidence Level
26	1.051*	± .005
	1.054	± .009
60	1.044**	± .004
74	1.031	± .007
87	1.034	± .007
99	1.027*	± .006
	1.032	± .007

*Four stage batch run
**Five stage batch run

1. Progress Report Alloy Development Project - ORNL-1238, December 31, 1951
2. Progress Report Alloy Development Project - ORNL-1306, March 31, 1952

[redacted]

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Each value listed in Table 1 was determined from mass spectrographic assays of twelve or sixteen separate samples.

In Figure 1, the quantity $\alpha - 1$ has been plotted against absolute temperature. The curve, $\alpha - 1 = -\frac{8.98}{T} + \frac{7428.7}{T^2}$ has been found to be useful for interpolation between the temperatures 20°C and 110°C. It was obtained empirically by fitting the equation

$$\alpha - 1 = \frac{A}{T} + \frac{B}{T^2}$$

to the data by means of the least squares method. This simple approximation can be shown to be in good agreement with theoretical values obtained by Urey on other systems through more elaborate calculations[3].

COLUMN DESIGN

Materials of Construction

The 1-inch D.T. pilot plant employed 316 stainless steel construction as an arbitrary choice. Subsequent tests on a laboratory scale indicated that mild steel was a more active catalyst for the reaction between the organic and amalgam phases at elevated temperatures than was 316 stainless steel.

Since the tests were conducted at 115°C and a reaction between the phases eventually was obtained in the absence of metals it appears desirable to obtain additional data to more closely define the maximum temperature that may be employed without reaction between the amalgam and EDA phases in the

3. H.C. Urey, The Thermodynamic Properties of Isotopic Substances, Liversidge Lecture, J.C.S. 1947, 562-581.

[redacted]

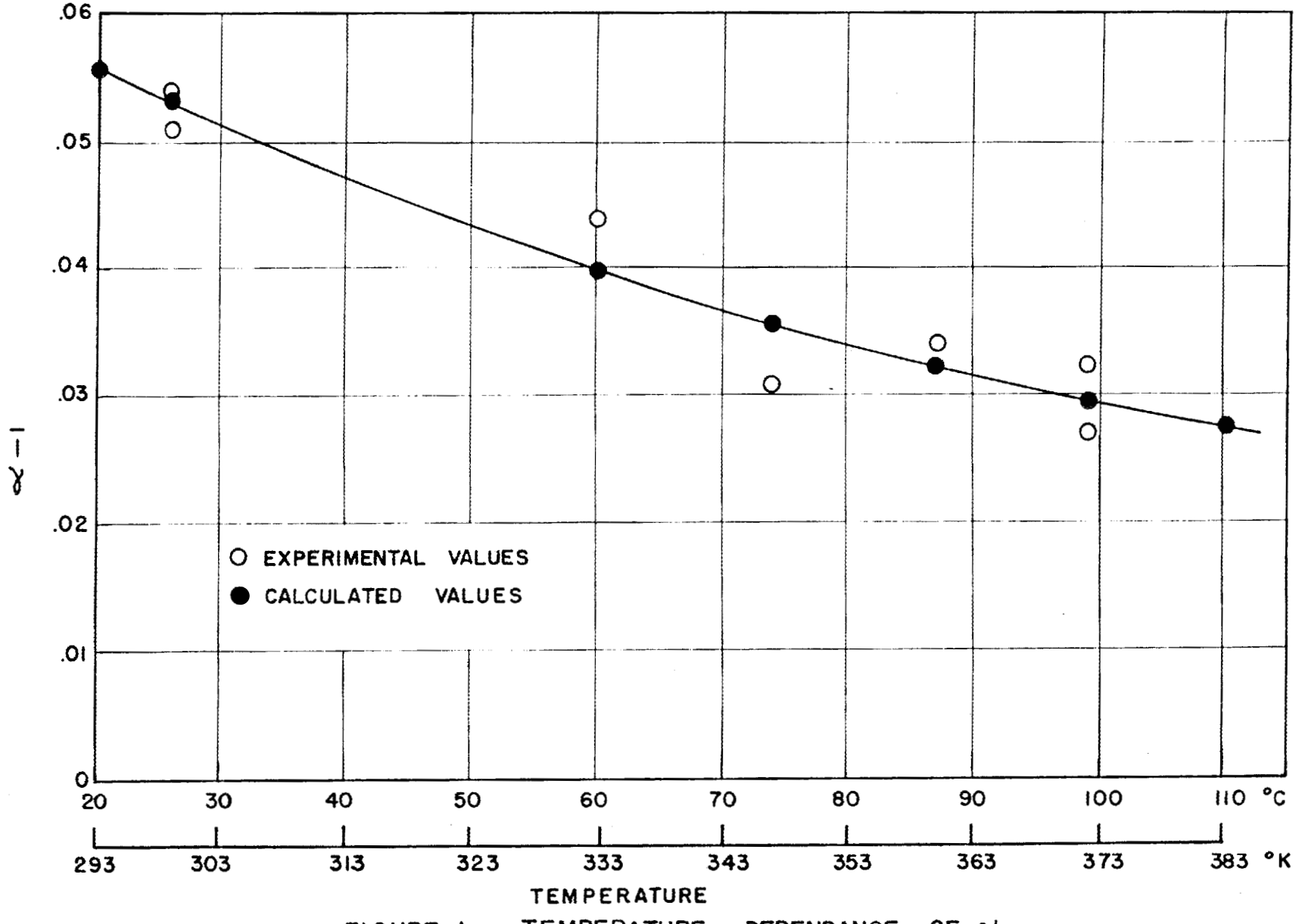

FIGURE 1. TEMPERATURE DEPENDANCE OF γ

presence of stainless steels (304, 316, etc.) and mild steel. In this connection the effect of water and of impurities in the amalgam and EDA phases on the rate of decomposition of the EDA phase should be evaluated at a single temperature in the range 100 to 120°C. Tests also should be conducted to determine if the mild steel will amalgamate in this system.

Should the results of the foregoing tests indicate that mild steel may be suitable as a construction material it should be tested in the pilot plant by installing mild steel screens in the short pyrex glass section at the midpoint on both the hot and cold columns to permit visual observation of its performance.

Optimum Screen Size and Spacing

In the 1-inch D.T. pilot plant the following screen sizes (all 316 stainless steel) have been employed: 60, 40, 24, 20, and 10 mesh in the cold columns and 60, 40, 30, and 20 mesh in the hot column. Indications are that the optimum size lies between 10 and 20 mesh in the cold column and between 20 and 30 mesh in the hot column. It is planned to continue the test of screen within the size ranges given in both the 1-inch D.T. columns and the 0.43 inch single column (reflux pilot plant) to serve as a guide in the design of large columns. The test program for the larger columns should also include a limited study of screen sizes; probably over the ranges in screen size given in the above.

Both the 1-inch D.T. columns and the 0.43-inch single column employ a spacing of 1-inch between screens. Tests are planned in which the spacing will be varied in order to determine the optimum spacing for the columns in both pilot plants. It appears likely that the optimum spacing will depend on the column size as well as the temperature in the column (hot vs cold) and to some extent on the method employed to support the screens. To obtain the desired scale-up factor it will be necessary to conduct appropriate studies in the larger pilot plant installations.

Optimum Height of a Column Section

Chemical Reflux. For a full-scale plant operating with chemical reflux the height of a column will depend entirely on the usual economic considerations and structural problems governing column construction and cascade design.

Dual Temperature. From the available theory on the dual temperature process it appears likely that, since the equilibrium curves (α-cold and α-hot) are very nearly straight lines, it will be possible to fix the column heights in accordance with economic considerations rather than by theoretical limitations. It will be necessary, however, to maintain control over the mass flow rates as closely as possible in order to achieve the maximum separation over a given length of column. A 1 percent deviation from the optimum L/V would reduce a 60 stage column to 59 effective stages while 2 percent deviation would reduce it to 55 stages.

The problem then resolves itself into: (a) finding the most accurate method for separately metering and controlling the amalgam and organic phases; (b) utilizing the available theory, calculate the economic optimum number of stages in a column section between stream junctions; and (c) by experiment, determine the number of actual stages in columns the length of which were estimated on the basis of the known accuracy of flow control and a reasonable estimate of the stage height from available experimental data.

The 1-inch D.T. pilot plant employs a column height of 24 feet which was the maximum head room available. The pilot plant was in operation before the mathematical theory was developed to its present state, in particular that part pertaining to the ratio of the flows of the two phases. For this reason the flow control studies have only recently been initiated. Until more data from the 1-inch D.T. pilot plant and the 0.43-inch single column (hot and cold operation) are available it is recommended that a stage height of 8 inches (based on 1-inch screen separation) be employed as a design value for the larger pilot plant columns.

Other Factors

Heat Transfer Data. Preliminary estimates were made of the cost of heating and cooling the inlet and exit streams in the D.T. process. The heat capacity of the amalgam and EDA phases are not known and in other respects the estimate was only approximate. For this reason the estimate should be made on a more thorough basis using experimentally determined values

of the heat capacity and viscosity data of both the amalgam and the EDA phases obtained over the range of temperature and concentration needed in this work.

Gaskets. The most satisfactory gasket tested to date is Garlock N. 7735 (asbestos filled with GRS rubber). A number of other materials commonly used for gaskets were tried and found unsatisfactory (ORNL-1238, page 27). It appears desirable to continue to find a gasket composition which will be inert to both phases and which will not catalyse the reaction between the phases at elevated temperatures.

PUMPING AND FLOW CONTROL

Pumping and flow control methods for both lithium amalgam and ethylenediamine must be developed. Flow control of both phases is equally important. Because a completely dry system is necessary and because it is important to minimize losses, highly efficient seals around pumping units are required.

High specific gravity of amalgam results in relatively high pumping pressures, even at intermediate heads (50-foot head of Hg corresponds to 300 psi). Thus, more serious problems are met in pumping amalgam than in pumping EDA. It might be possible to place amalgam pumps at different levels in series if necessary to reach the top of high columns.

Accuracy requirements in flow rate and concentration of lithium are very great, creating a control problem which is almost unique in chemical production operations. This is particularly true in the D.T. system. Flow control in the reflux system should be good, but the extreme accuracy of the D.T. system is not required. The high accuracy requirement results from the great influence on separation of the ratio of lithium throughputs in the two phases. This may be shown on the McCabe-Thiele diagram by an operating line whose slope is the ratio of lithium throughputs in the two phases and which must lie between the equilibrium curves of the hot and cold systems. These curves are very close together since the coefficients are not far apart and both very near unity. A slight deviation in slope of the operating line causes "pinching" and consequent ineffectiveness of separation stages. It may be shown mathematically that depending on the number of stages of a given unit, a fluctuation in throughput of no more than 5% may result in reduced theoretical production of a unit of from 25-50%. These are approximate figures only, and the mathematics is being refined at the present time.

It may be seen that accurate control of L/V (throughput ratio, lithium in amine to lithium in amalgam) may be obtained only by accurate control of two separate factors: flow rate, and concentration of lithium, in each of two separate phases.

In joining several units in series to form a cascade, there will be stream junctions which also must be controlled very carefully in order to maintain good flow control in the separate stage units.

To date, development of pumps and controls has been limited. A test loop has been built in Room 25, 9733-1, to evaluate different types of pumps handling amalgam and to obtain primary information on instruments for measuring and controlling flow rate of amalgam. Tests are being run at the present time on a standard chemical pump, the Worthington 3/4-CG-1 stainless steel pump. Other pumps which are being purchased for later testing are (1) the Chempump, which is a newly marketed canned rotor pump, and (2) a special gas-filled canned rotor pump being designed by Allis-Chalmers Corporation. Pumping in the 1-inch pilot plant has been handled by Milton-Roy reciprocating pumps, which are good by ordinary standards but not satisfactory in this case, and Lapp Pulsafeeders which give improved operation by virtue of isolated pumping chambers and spring-loaded check valves for improved uniformity of flow. It is expected that, by using Lapp Pulsefeeders in the range of low flow rates, and the Allis-Chalmers canned rotor centrifugal pumps in the range of higher flow rates, the pumping problems for both amalgam and ethylenediamine may find solution. Centrifugal pumps seem most appropriate for

operation in the higher flow ranges, but are not believed suitable for operation in pulse columns smaller than about three inches in diameter.

A magnetic induction instrument for measuring and controlling flow rate is being tested in the 1-inch pulse column. This instrument was designed by the Vitro Corporation and is being tested in cooperation with representatives of that company. This work represents only a beginning of the development work which is needed on flow control. No work has been done to date on actual instrumental control of streams based on measurement by flow meters.

A preliminary estimate by instrument engineers of the ultimate accuracy which may be expected of flow control by instrumentation is plus-or-minus 1 percent. Defining and achieving the required degree of accuracy is a development task of considerable magnitude.

CHEMICAL REFLUX

General Considerations

Operation of a cascade employing chemical reflux requires the following: (a) where the cascade narrows above the feed point, the lithium content of that portion of the total amalgam flow in excess of that continuing on in the narrowed column must be transferred from the amalgam to the incoming (lithium free) EDA which is recycled from the reflux operation at the bottom of the cascade as described in (b); and (b) the total lithium content of the EDA phase leaving the stripping section at the bottom of cascade must be removed and all except the waste stream must be reacted with the incoming recycle mercury from the reflux operation described in (a) to form lithium amalgam. The various methods that appear to be feasible for effecting reflux are discussed in the following.

Transfer of Lithium from Mercury to EDA

Displacement with Sodium Chloride. The results of laboratory tests in which the lithium content of the amalgam phase was displaced with sodium by contacting lithium amalgam with an EDA slurry of sodium chloride indicate the possibility of effecting reflux in this manner. The laboratory studies should be extended to define the effect of temperature, agitation (or method of contacting), and particle size of the NaCl on the rate of the displacement reaction.

Tests on a larger scale in which a 0.5-inch pulse column is employed to effect countercurrent contacting of the amalgam and EDA NaCl slurry are in progress.

Displacement with HCl or NH_4Cl. The results of a limited number of laboratory tests in which a part of the EDA was converted to EDA·HCl by means of anhydrous hydrogen chloride prior to contacting it with lithium-amalgam indicated that this method may be feasible for effecting the desired reflux.* Consequently, it appears desirable to conduct the necessary laboratory and small-scale development work to permit evaluation of the method in comparison to the sodium chloride method.

The use of ammonium chloride instead of hydrogen chloride has been suggested. In this case the EDA presumably would not enter into reaction; instead, an ammonia-amalgam would be formed which, although semistable, may serve to displace the lithium in the desired manner. It is recommended that exploratory tests be conducted to demonstrate the proposed reaction and, if warranted, the necessary development to permit evaluation of the method should be carried out.

Transfer of Lithium from EDA to Mercury

Evaporation and Salting Out Method. A method involving vacuum evaporation of the EDA phase in a salting out type

*In one series of tests employing mechanical agitation the resulting amalgam was expanded and semisolid. In subsequent tests using shaking by hand there was no evidence of an expanded amalgam

evaporator, by-passing an aliquot portion of the concentrate to a crystallizer, and processing of the resultant LiCl·2EDA to yield EDA recycle streams and LiCl has been proposed as one means for effecting the desired recycle utilizing standard process equipment. Preliminary process calculations have been made and a tentative flow sheet is available. A discussion of the assumptions made and of general considerations follows.

Under the conditions assumed for the flow diagram a salt-out type evaporator will not be necessary as the concentration in the evaporator is such that no crystallization of salt occurs. If operation with higher concentration is desired, it may be necessary to employ two evaporators in series with the more concentrated liquor in a salting out type evaporator. The use of the EDA itself to fill the barometric leg requires that essentially all noncondensables be absent; this implies a stable and essentially pure EDA phase. The formation of a solvated solid phase (LiCl 2EDA) requires further processing of the salt to remove the EDA if it is not practical to carry out the crystallization at a temperature that will provide EDA free LiCl. The additional processing shown on the flow sheet consists of a fluidized reactor into which is fed the wet solvate countercurrent to benzene vapor. It has been shown in the laboratory that the solvate decomposes into EDA and LiCl at a temperature of about 200°C. It may also be feasible to employ spray drying technique without appreciable loss of the expen-

sive solvent since the quantity of materials is relatively small. In the first case a follow-up distillation step to separate the EDA from benzene is required; preliminary estimates indicate that about 20 plates will be necessary to reduce the benzene content of EDA to about .05 mole percent. An estimate of the cost of carrying out the reflux method should be made and, if economically attractive, the necessary data and test work should be carried out to demonstrate feasibility and to provide the basis for a more accurate cost analysis.

Direct Electrolysis. The possibility of employing a direct electrolysis of lithium from the EDA phase into the amalgam phase appears to hold promise provided a cell can be designed to employ a mercury anode as well as a mercury cathode. One possibility is that of employing a plastic trough filled with mercury (as the anode) suspended in the EDA phase above Li amalgam. Presumably the reaction would be:

Cathode: $Hg + Li^+ \longrightarrow Hg_xLi$

Anode: $1/2\ Hg + Cl^- \longrightarrow 1/2\ HgCl_2$* (insoluble)

The $HgCl_2$ may then be utilized in the opposite reflux operation in the same manner as NH_4Cl. The necessary studies should be carried out to permit evaluation of the method from a technical standpoint.

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* If a double salt such as $LiCl \cdot xHgCl_2$ formed in the anode pool it would be necessary to devise means for transferring the LiCl to the amalgam phase.

By Other Methods. Precipitation of the Li^+ from the amine may also be possible Further laboratory work on the carbonate precipitation with EDA H_2CO_3 should be done.

Lithium Trimethyl Stannide

Work is now in progress to determine the potentialities of compounds of the type LiR_3Sn, as suggested by Chas. A. Kraus. Only very small-scale and semiquantitative experiments have been possible so far. The compound in which R is CH_3 has been prepared and found to give EDA solution one-half to one molar in concentration at room temperature. The compound was prepared in EDA solution by the reaction of lithium amalgam with the dimer of trimethyl tin.

$$2Li(Hg)x + \left[(CH_3)_3Sn\right]_2 \longrightarrow 2\ Li\left[Sn(CH_3)_3\right] + 2xHg$$

This system may establish itself as an equilibrium mixture though it seems fairly certain that the reaction goes, for all practical purposes, to completion as written. This reaction has been found to proceed very slowly even with vigorous agitation. The lithium trimethyl stannide solution in EDA was found not to be stable at 100°C. Electrolysis of the EDA solution, using a platinum anode and mercury cathode, proceeded quite smoothly at low current density, 10 to 20 ma per cm^2, forming lithium amalgam and the heavy oily insoluble dimer of trimethyl tin. At higher current densities and temperatures, side reactions occurred but the observations were obscured by uncertainty as to the initial purity and composition of the system.

PREPARATION OF THE EDA PHASE

General Considerations

The quantity of EDA required in either the chemical reflux or the D.T. system will be that required to fill the plant prior to the start of operation plus a sufficient quantity to make up process losses over a reasonable period of time. The interstage flow of the EDA phase on the basis of a 1 X production rate will be about 40 gpm for chemical reflux and 170 gpm for the D.T. system. On the assumption that the maximum purity of the EDA that will be commercially available is 99 per cent or less it is apparent that: (a) it will be necessary to prepare essentially anhydrous material from commercial grades since any remaining water will react with the lithium amalgam to form lithium hydroxide which is slightly soluble in EDA; and (b) since the present cost of the 77 percent grade is $0.47 per pound of EDA content and that of the 98-99 percent grade is $1.00 per pound of EDA, the grade to be purchased as well as the method employed for preparing anhydrous material will depend to a large extent on the total quantity desired of enriched product and on the loss of EDA during operation of the cascade. The possibility of designing a cascade to maintain the EDA losses at no more than 0.1 percent of the interstage flow appears to be reasonable at this stage. For estimating purposes a production rate of 10 X (Li^6 product) is recommended.

Drying EDA

The possible methods for preparing essentially anhydrous EDA that have been considered to date are discussed in the following.

Basic Oxides. Essentially anhydrous EDA has been prepared by contacting the 99 percent grade with barium oxide. Conversion of the resulting barium hydroxide to the oxide involves a somewhat complicated procedure and for this reason work on the method was not continued beyond the preliminary stages. Barium peroxide forms a hydrate containing $8H_2O$ and some exploratory tests should be carried out to determine if the desired hydrate can be formed without oxidation of the EDA.

Sodium hydroxide was partially effective in that the water content of $EDA \cdot H_2O$ was reduced from 23 percent to 4 percent. Additional treatment of the 4 percent product with NaOH was not effective.

The oxides of aluminum (activated) and calcium were not effective in the removal of water from EDA. However, the tests involving lime were not extensive and additional work should be carried out to more thoroughly explore its possibilities.

Calcium Carbide and Metallic Sodium. Calcium carbide reacted with the EDA hydrate to form acetylene without apparent effect on the EDA. It is not known whether or not the solid phase was the oxide or the hydroxide of calcium. Gas evolution was copious and the resulting EDA was essentially anhydrous.

Metallic sodium was effective in dehydrating EDA. However, a significant portion of the EDA also was involved in the reaction, and its over-all recovery was at times as low as 60 percent of that charged.

Azeotropic Distillation. Both benzene and 2-methyl furan were effective in dehydrating EDA when azeotropic (water azeotrope) distillation was carried out. In both cases the aqueous content of the azeotrope is low and for this reason it appears that a continuous countercurrent stripping operations* may be more economical than azeotropic distillation.

Drying EDA With Ethylene Glycol. Preliminary experiments show that water can be separated from EDA by extractive distillation using ethylene glycol as a solvent. One hundred ml. ethylenediamine monohydrate and 150 ml. ethylene glycol were placed in a flask and fractionated in a 5/8-inch diameter 90-inch high column. Water came over first until there was no more water in the still pot. At this point, the water holdup in the column combined with the EDA fraction to give an $EDA \cdot H_2O$ fraction. However, this can be overcome by using the regular extractive distillation technique. The EDA-ethylene glycol mixture remaining in the pot was easily separated by distillation of the EDA. This work should be continued to

*In a stripping operation, temperatures are employed so that the liquid which contains the volatile impurity to be removed is not volatilized to an appreciable extent.

provide data for technical and economic evaluation of the method.

Process Development. Results of the exploratory work on the various methods indicates that the azeotropic distillation and stripping* are likely to be less expensive than other methods with the possible exception of calcium carbide treatment of 98-99 percent grade EDA. Sufficient data should be obtained to permit preparation of a cost estimate for these two methods which would serve as a basis for evaluation of methods which may be proposed in the future.

Type of Lithium Salt

Preparation of the EDA phase involves simply the contacting of the desired salt with anhydrous EDA in a suitable dissolver. The salts which are sufficiently soluble in EDA and relatively stable against Li amalgam are the chloride, perchlorate, and the formate. Since these salts are appreciably more soluble** at elevated temperatures and the rate of solution increases with an increase in temperature the solution temperature presumably would be somewhere between 50 and 100°C.

Because, in the reflux process, it will be necessary to convert the lithium contained in the amalgam phase to the

*See footnote on Page 21.

**Li formate is 1.9 molar + Li perchlorate at 3.8 molar at room temperature. Since these solutions are viscous, it was not considered necessary to study the solubility further.

lithium salt dissolved in the EDA phase, it appears that lithium chloride only may be used without the complicating steps involved in regenerating any other lithium salt. This restriction does not apply to the D.T. process and either the formate (if stable) or the perchlorate (if safe) may be used in place of the chloride.

Propylene Diamine

Propylene diamine (1-2 diamine propane) possesses several properties that indicate it may prove more satisfactory than ethylene diamine. It is reported in the literature that water and PDA can be separated by direct distillation. Preliminary tests in this laboratory confirm this statement. Lithium chloride has been found to be considerably more soluble in anhydrous PDA than in EDA. Solubility of LiCl at 21.3^{o}C is .86 molar and at 25°C, 1.09 molar. The solubility is changing quite rapidly with temperature in this region. No deterioration has been noticed in static sealed bomb tests of the LiCl in PDA vs Li amalgam system at 100°C for 12 days in the presence of stainless steel wire. Limited data from a single stage separation experiment show that the isotopic separation factor is of the same magnitude as that of the corresponding EDA system. Further work on PDA is under way.

PREPARATION OF AMALGAM PHASE

Amalgam Preparation

The quantity of feed required for a full-scale plant operating on either the D.T. or chemical reflux method will be about 125 pounds of lithium per day (natural abundance) for a product rate of 1X and a waste concentration of about 5 percent Li^6. This corresponds to a flow rate of about 11 liters per minute of 0.5 molar amalgam.* Since the Mathieson Chemical Company has developed a cell suitable for preparing lithium amalgam from LiCl brine it is presumed that no additional development work on the large scale will be needed. For operation of pilot plants it will be necessary to build units capable of preparing lithium-amalgam feed at the desired rate. A 3.5-inch wide, 3-inch deep, and 10.5 feet in length amalgamaker has been used successfully at Y-12 on small-scale tests. The unit contains 40 agitators and employs carbon anodes with the amalgam serving as the cathode. Its capacity was about .2 liters/minute of 0.5 molar amalgam and a 300 ampere, 12-volt D.C. rectifier provides the necessary power. A detailed description as well as the performance data for the Elex Pilot Plant unit are given in ORNL-1254.

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*The possibility of utilizing the EDA phase as the feed also exists and the feasibility should be evaluated after the necessary information is available.

The possibility of electrolyzing the lithium content of the EDA phase into mercury to form lithium amalgam is discussed under the section on chemical reflux.

Drying Amalgam

To minimize the possibility of water entering the system, it will be necessary to incorporate a drying step in the pilot plant layout involving the removal of aqueous lithium hydroxide from the amalgam phase prior to its introduction into the pulse columns. Some of the factors to be considered are discussed in the following:

General Considerations. The quantity of water entrained in the amalgam as lithium hydroxide solution under ordinary conditions of cell operation should be no more than 0.3 cc per liter of amalgam. Laboratory studies have shown that: (a) the water portion of the aqueous phase reacts with lithium amalgam to form lithium hydroxide; and (b) mixing of most organic liquids with lithium amalgam results either in the formation of an emulsion which can be broken only be adding water or in reaction between the phases. It is not feasible, for instance, to dry the amalgam in a short section of a pulse column countercurrent to an organic liquid which has a high affinity for water. It may be economically feasible, however, to utilize a relatively small volume of the EDA phase for drying the amalgam outside the column.

One-Inch D.T. Pilot Plant Method. In the 1-inch D.T. pilot plant the amalgam is siphoned through a U-tube from a stilled section of the cell. The amalgam is then washed with ethyl alcohol. Data from past runs indicate that this method was not completely effective; in some runs the decrease in lithium concentration of the amalgam in the system amounted to as much as 10 percent over the first six hours while in other runs the decrease was negligible.

A variation in the above method has been suggested which involves: (a) withdrawal of the amalgam from the cell at a point near the bottom of the cell through a nickel tip which is readily wetted by the amalgam; and (b) transfer the amalgam through a barometric leg into a tank (possibly agitated) which is maintained at about 50°C under a vacuum. It would also be necessary to withdraw the dried amalgam through a second barometric leg and to provide means for removal of the solid lithium hydroxide from the surface of the amalgam at intervals.

PRODUCT AND WASTE STREAMS CONVERSION

General Considerations

In either the D.T. or the C.R. process it will be necessary to operate a cascade with lithium waste withdrawal as well as with product withdrawal. Choice of the phase from

which to withdraw the product and waste streams for the D.T. process depends entirely on the ease with which lithium solute is recovered from the solvent. This also is true of the product stream of the C.R. process but the waste stream must be withdrawn from the EDA phase because of the necessity for reflux at the 7-end of the cascade as previously explained.

Tests carried out in connection with the Elex pilot plant show that the amalgam phase is readily and completely decomposed in contact with metallized graphite in contact with water. For this reason no consideration has been given to withdrawing lithium (either product or waste) from the EDA phase.

Amalgam Decomposer

In the commercial production of sodium hydroxide the sodium amalgam is decomposed by percolating it over metallized (Fe) graphite packing countercurrent to water. It was decided to build a test unit employing the principle of the sodium amalgam decomposers to determine the feasibility of using it as a lithium amalgam decomposer in the Elex pilot plant. The unit was 12 inches in diameter and 34 inches in height and it was filled with + 1/4, -1 mesh graphite which previously had been wetted with concentrated $FeCl_3$ solution and then heated to 900°C in a muffle furnace: The amalgam

flowed over a distribution plate at the top, countercurrent to distilled water which was introduced at the bottom of the unit. The stripped mercury was recycled back to the 7-refluxers while the lithium hydroxide solution was pumped to the 6-refluxers. The maximum capacity of the unit has not been established; however, it operated successfully over a 150-hour period with a lithium flow rate in the amalgam phase equivalent to 2 moles per minute.

It may be desirable to obtain more accurate data on the capacity of the metallized graphite in small scale units. It is expected that continued operation of the Elex pilot plant unit will serve as the basis for estimating the life of the catalyst.

Mercury Purification. The need for maintaining purity requirements on mercury has not been established. Since Na and K are present in commercial lithium hydroxide and readily electrolyze into mercury to form more stable amalgams than does lithium, it appears desirable to incorporate an acid wash tower and a follow-up water wash tower in the pilot plant layout to minimize the possibility of accumulating significant quantities of the metals in the system. This arrangement has proved to be satisfactory in the Elex pilot plant. The two wash towers would be installed in the mercury recycle path between the 6-refluxers and the amalgam cells.

The same problem may be encountered when using lithium chloride brine as feed to the cells. At the earliest opportunity information should be obtained on the quantity of Na and K in commercial lithium chloride.

Stability of the EDA Phase*

The results of laboratory studies in which the mixed EDA and amalgam phases were sealed in small glass "bombs" after which each bomb was held at a constant temperature for a period of several weeks indicated that decomposition of the EDA phase started at a temperature of about 120°C. The EDA phase alone was stable up to 180°C.

During D. T. pilot plant operations the hot column was usually maintained at a temperature of 100°C. At the end of a run the EDA phase was not drained and to start a new run a sufficient quantity of freshly prepared EDA phase to fill the system was added (approximately 1/3 of total volume). Although there were no runs of longer duration than 71 hours, the cumulative time for part of the EDA phase was somewhat longer than that.

In view of the above it appears desirable to continue the study of the effect of temperature on the decomposition of the EDA phase in contact with amalgam. This may be done

* EDA-lithium chloride solution.

by carrying out long runs in the D.T. pilot plant with a minimum of sampling or in a separate column designed specifically for the studies. In the latter, a test loop could be employed, consisting of a 1-inch column of similar construction to the hot column of the 1-inch D.T. pilot plant, with no attempt at isotope separation.