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Development Requirements
TO: R. E. Blanco
FROM: J. C. Bresee
J. C. Suddath

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CLASSIFICATION CHANGED TO
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DATE 7-18-56

J. C. Suddath

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218-1

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-H. F. Canale
Chief, Declassification Branch

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In order to coordinate the Metallex Process development activities of the Chemical Development and Unit Operations Sections, suggestions for experimental programs are presented. Before specific proposals are given, it is desirable to review the dry-salt process flow sheets either under active consideration or under consideration as alternates. The various flow sheets will be discussed only from the stage of ThCl_4 feed to a dry-salt contactor through the formation of a compacted thorium quasi-amalgam suitable for feed to a retorting operation.

Uni-Contact Aqueous Process

In Figure 1 is presented the flow sheet of the process under active consideration. Various operations which will be discussed in more detail later are identified by numbers on this as well as the other figures.

In general the process is quite similar to the "wet" or PDA process which the dry-salt process is to replace, with one major difference. Since in the PDA process the unreacted ThCl_4 remains in the light PDA phase after contact with the sodium amalgam, the two phases may be separated by decantation and two or more contacts may be made between the remaining ThCl_4 and fresh amalgam. The dry-salt reaction depends upon intimate solid-liquid contact and the unreduced thorium salt necessary leaves the reactor when the amalgam is removed. Also accompanying the amalgam is a dispersed form of a product of the reduction, NaCl as well as colloidal amalgam.

Depending upon the efficiency of the reduction in the dry-salt contactor, a certain percentage of the ThCl_4 feed will be washed from the amalgam in the wash column. All of this thorium must be recovered by a procedure of precipitation and filtration, resulting in an oxalate which would be recycled to a chlorination process.

A separate coagulation step for the washed amalgam may or may not be necessary. It is possible that the contactor itself might be operated first at a high rate of shear to give effective solid-liquid contact and later with mild agitation to allow the growth of thorium-quasi amalgam crystals. The filtration of the coagulated quasi could be carried out in a filter press similar to a Carver press, in which both filtration and cold pressing could be accomplished. Normally such presses are not designed to permit washing of the filter cake.

218 2
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FIGURE 1.
METALLEX DRY-SALT PROCESSES
UNI-CONTACT AQUEOUS PROCESS

TH RECOVERY (6)

Mercury from the filtering and pressing operations would be recycled to an amalgam make-up step. Sodium could be added to the mercury either mechanically or electrolytically. A comparison of the economics of the two alternate processes is being made by the Process Design Section.

Multi-Contact Non-Aqueous Process

Figure 2 shows the first of two alternate dry-salt processes. The basic difference between the alternate processes and first process discussed is the separation of unreacted thorium tetrachloride and product sodium chloride from the sodium amalgam containing thorium-quasi amalgam by filtration. This separation would be accomplished by operating the contactor to produce a thorium-quasi amalgam of very fine particle size, compared with the particle size of the reactant and product chlorides.

Such a separation would permit multi-stage contacting of the feed in the same way that multi-stage contacting is possible in the PDA, or wet, process. In the wet process, unreacted ThCl_4 is maintained in the reactor in the PDA phase while the amalgam phase is drawn off the bottom. Several stages of contact are possible in the same reactor merely by recharging with fresh sodium amalgam. In the alternate dry-salt process the decantation separation is replaced by filtration.

In Figure 2, an alternate to multi-stage contacting is also shown. The salt cake from the primary filtration of the reactor contents would be leached with absolute ethanol to remove selectively unreacted ThCl_4 . The ethanol would be separated from the ThCl_4 by vacuum drying, and the salt would be recycled to the reactor feed stream. Obviously if such a recycle process were successful for the treatment of primary filter cake, it could equally well be applied to the purification of feed material to the reactor.

A separate coagulation step obviously will be necessary in a process which depends for its success on the production of a very finely dispersed thorium-quasi amalgam. In the process labeled "non-aqueous", the filtration of the coagulated quasi amalgam would be carried out without the prior removal of the sodium by acid or water washing.

Instead, the sodium would be washed from the filter cake by mercury. The wash mercury would then be regenerated by an external aqueous washing operation.

218- 4

DECLASSIFIED

FIGURE 2

The mercury washing process offers the double advantage of separating the thorium from the oxidizing environment of aqueous processing and permitting the recycle of a sodium amalgam filtrate stream for enrichment in the amalgam make-up system.

Cold pressing of the mercury-washed quasi cake would provide feed to the retorting operation.

Multi-Contact Aqueous Process

In Figure 3 is shown the second alternate dry-salt process. As the name would indicate, the multi-contact aqueous process is essentially a combination of the first two processes. The hot filtration step, discussed in connection with the second flow sheet, is included in this process. In addition, the filtrate from this step would be acid or water washed to remove the sodium from the thorium-bearing mercury phase.

A coagulation step will probably be necessary following the washing operation, for the same reasons outlined under the second process discussion. The filtering and cold pressing steps should be similar to those proposed for the first process.

The aim of the second alternate dry-salt process would be to obtain the advantages of the multi-stage or recycle contacting of the multi-contact non-aqueous process while retaining the proven advantages of product purity resulting from acid or water washing of the hot filtrate. The value of acid washing for product purity has been demonstrated not only in small-scale laboratory studies of dry-salt contactors by the Chemical Development Section but also in the production of thorium quasi-amalgam by the PDA route in the Unit Operations Section.

Proposals for Process Development Studies

The following are specific proposals for process development studies. The numbers designating the operations refer to the figure and circled numbers mentioned earlier.

<u>Item</u>	<u>Operation</u>	<u>Process Development Requirements</u>
1	1-1	*a. Determination of effect of variables; Na amalgam molarity, Na/ThCl ₄ ratio, temperature, and time on tetrachloride reduction in a small-scale dry salt contactor.

218-

6

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FIGURE 3.

EX DRY-SALT PROCESSES

-CONTACT AQUEOUS PROCESS

NOTE: DASHED LINES INDICATE ALTERNATE PROCESS FLOWS.

218- 7

[illegible]

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<u>Item</u>	<u>Operation</u>	<u>Process Development Requirements</u>
		*b. Study of effect of contactor design on efficiency of tetrachloride reduction; determination of scale-up data. <i>Brace</i>
2	1-2	a. Study of performance of amalgam wash column, in the presence of unreacted and product salt. Comparison of spray and conductor-packed column, using HCl and water. <i>Suddeth + Brace</i> b. Determination of effect of acidity and oxygen concentration on thorium oxidation during washing operations.
3	1-3 (3-4)	*a. Study of effect of time, temperature, and agitation on thorium quasi coagulation in washed amalgam; determination of filtration characteristics of resulting coagulent. *b. Comparison of coagulation in reactor of unwashed amalgam with that of washed amalgam.
4	1-4 (3-5)	Study of combined filtration-cold pressing operation of thorium quasi-amalgam (e.g., Carver press). <i>Suddeth</i>
5	1-5 (2-5) (3-6)	a. Cost comparison of electrolytic cell with direct addition of sodium for amalgam make-up. b. Engineering development of direct-addition process, if economically advisable. ?
6	1-6	*Chemical and engineering study of thorium recovery process. <i>Brace &/or Suddeth</i>
7	2-2 (3-2)	*Study of separation of unreacted and product salt from amalgam; effect of filter design on hold-up of thorium-quasi on filter cake. <i>Brace (other filters)</i>
8	2-3	*Study of effect of time, temperature, and agitation on thorium quasi coagulation in unwashed, filtered amalgam and determination of filtration characteristics of resulting coagulent.

218- 8

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<u>Item</u>	<u>Operation</u>	<u>Process Development Requirements</u>
9	2-4 2-6	a. Study of the removal of sodium from thorium quasi filter cake by mercury washing. b. Study of performance of wash column for removal of small amounts of sodium from mercury, with recycle of dry mercury. ?
10	2-7	Chemical and engineering evaluation of ethanol recycle process. <i>Bruce</i>
11	3-3	Study of performance of amalgam wash column, using hot filtered amalgam feed. <i>Suddath</i>

NOTE: *Priority items

Suggested Development Responsibilities

<u>Item</u>	<u>Sections</u>		
	<u>Chem. Dev.</u>	<u>UNOP</u>	<u>Design</u>
1a	A		
1b		A	
2a		A	
2b	P		
3a	P		
3b	P		
4		P	
5a			A
5b		P	
6	P	P	P
7		A	
8	P		
9a	P		
9b		P	
10		A	
11		P	

NOTE: A - active, P - proposed

THIS MEMORANDUM HAS BEEN READ AND APPROVED BY THE METALLEX PLANNING COMMITTEE+

218- 9

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