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by A. E. Smith .

FLOWSHEET NO. 1 - CESIUM ISOLATION AND PACKAGING

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Process Equipment Development
Chemical Development
Chemical Research & Development
HANFORD LABORATORIES OPERATION

May 20, 1957

HANFORD ATOMIC PRODUCTS OPERATION

RICHLAND, WASHINGTON

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FLOWSHEET NO. 1 - CESIUM ISOLATION AND PACKAGING

INTRODUCTION

The objectives outlined in HW-48919, "Fission Product Isolation and Packaging Equipment Development Program", by A. E. Smith, February 28, 1957, offered a target date of May 1, 1957 for completion of the first engineering flowsheet defining a process to convert an aqueous slurry of cesium-zinc-ferrocyanide into a dry, radiation-stable compound. This document presents such a flowsheet and certain of its features are discussed in terms of workability, practicality, and safety.

SUMMARY AND CONCLUSIONS

An engineering flowsheet has been prepared for the conversion of an aqueous slurry of cesium-zinc-ferrocyanide into a dry cesium chloride product by the calcination process. Flowsheet No. 1 defines a six-step batch-type calcination operation for processing the slurry into a dry powder for offsite shipment in bulk containers.

Some of the advantages to this process are as follows:

1. Product losses are expected to be small. These losses are estimated to be less than 0.03 percent.

2. The equipment required to process a given number of curies per batch appears to be relatively small, compact, and simple.

3. The process does not impose severe requirements for materials of construction.

4. Requirements for process control and instrumentation are expected to be simple.

The disadvantages of this process are as follows:

1. The cesium-zinc-ferrocyanide precipitate is not considered economically filterable; hence, the separation of solids from liquids is encumbered.

2. The process, as outlined, is potentially hazardous because of the possible nitrate carry-over with the influent slurry. This nitrate may cause a rapid reaction in the calcination step.

It is concluded that this flowsheet offers a satisfactory scheme for isolating radiocesium if the process is modified to preclude the possibility of nitrates or other unwanted oxidants from reaching the calcination step.

DISCUSSION

This flowsheet is based upon the requirements for the batchwise processing of 100 gallons of aqueous slurry containing 0.05 molar $Cs_2ZnFe(CN)_6$ precipitate, centrifuged from neutralized 1WW, and redispersed in water to render it transferable by pump or jet. The flowsheet defines a six-step operation for processing the slurry into a dry powder packaged for offsite shipment in bulk containers. The six processing steps are as follows: (1) Drying the $Cs_2ZnFe(CN)_6$, (2) calcining, (3) leaching, (4) conversion to the chloride, (5) drying and storage of product, and (6) packaging.

Process

The six steps in the outlined process are discussed in the following sections:

1. Drying the $Cs_2ZnFe(CN)_6$

A drying step precedes calcination and consists of separating liquids from solids. Filtration is impractical, as will be discussed later; however, separation may be accomplished by centrifugation, evaporation, or both. The 100 gallons of slurry contains 833 pounds of water and requires a minimum input of 930,000 Btu's if all the water is removed by evaporation.

2. Calcination

The calcination step converts the $Cs_2ZnFe(CN)_6$ to a mixture of oxides of cesium, zinc, and iron from which the cesium can subsequently be isolated by a leaching step. The $Cs_2ZnFe(CN)_6$ must be heated to about 500 C in air to initiate the reaction, thereafter the exothermic reaction is expected to require an excess of air for cooling. An estimated 2310 cubic feet of air at 18 C (300 percent excess) is required to completely oxidize the process material and to keep the bed temperature below an average of 800 C. Evolved from this reaction are an estimated 8650 cubic feet of off-gases which must be discharged to the stack through a filter.

3. Leaching

The calcined solids are leached with water to separate the cesium for further processing. Four leaches with 1-3/4 gallons of water each are expected to remove 99.97 percent of the cesium from the solids. The cesium lost is that contained in the water resident with the zinc and iron oxide waste. It is expected that these solids will be filterable. If the waste oxide solids are dried for disposal, the gamma radiation due to lost cesium will amount to about 7-1/2 curies per pound.

The leaching operation converts cesium oxide to cesium hydroxide with an accompanying evolution of heat. An anticipated average 60 C temperature rise is expected during this process, neglecting heat losses to the vessel and surroundings; however, realistically, heat will be transferred from the solution and a temperature of 75 C indicated on the flowsheet may not be attained.

It appears practical to concentrate the composite leach liquor before converting the cesium hydroxide to the chloride. A ten-to-one reduction in volume requires a minimum of 60,000 Btu's to drive off about 50 pounds of water.

4. Conversion to Chloride

The cesium hydroxide received from the concentrator is converted to cesium chloride by the addition of concentrated hydrochloric acid. As an alternate means, dry hydrogen chloride gas may be added to the concentrate to achieve the same result. By either method, the resulting product will be an aqueous water solution of cesium chloride with an excess of HCl.

5. Drying and Storage of Product

To ensure a radiation stable product, the cesium chloride must be completely dry. Drying this product also reduces its corrosiveness towards storage and shipping containers. If an aqueous solution of cesium chloride is treated in accordance with the flowsheet, the minimum heat input requirement is about 13,000 Btu's to drive off the water and excess HCl. The crystalline cesium chloride will probably require mechanical working to free it from evaporator surfaces and to empty it into a hopper. To preclude water absorption, the temperature of the product should not be permitted to fall below 120 C.

6. Packaging

The dry cesium chloride powder is to be packaged into sealed bulk containers for offsite shipment. Powder handled in contact with air should be kept free of moisture to ensure a dry product. The estimated volume of dry cesium chloride produced from 100 gallons of 0.05 molar $Cs_2ZnFe(CN)_6$ slurry is about 0.15 cubic feet and will have a gamma activity of about 1.73×10^5 curies.

Properties of the $Cs_2ZnFe(CN)_6$ Slurry

Some of the properties of the aqueous slurry of $Cs_2ZnFe(CN)^6$ precipitate, pertinent to this flowsheet, are discussed in the following sections:

1. Filterability

Large-scale filtration of the $Cs_2ZnFe(CN)_6$ precipitate appears impractical in view of low filtration rates observed in laboratory tests. Under a differential pressure of approximately 60 cm. Hg, the filtration rate for centrifuged precipitate dispersed in two volumes of water was 2.8 $ml/hr/cm^2$ with a cake depth of 1 mm on a fritted glass filter, 4 to 5.5 micron porosity. The same type of solid dispersed in ten volumes of water and digested for four hours at 100 C filtered at a rate of 5.4 $ml/hr/cm^2$ under the same conditions except for a coarser filter media (10 to 15 micron porosity). Increased cake depth decreases the filtration rate. It might be noted that the $Cs_2ZnFe(CN)_6$ for these tests was precipitated from a solution much more concentrated than the expected 1WW. Previous experience points toward even slower filtration when the solid is precipitated at 1WW cesium concentrations.

2. Effect of Nitrates During Calcination

The $Cs_2ZnFe(CN)_6$ precipitated from 1WW has been found to contain nitrate which when taken to the calcination step may result in a reaction of explosive proportions. The solids as centrifuged from 0.1 molar $NaNO_3$ solution showed little or no tendency for rapid reaction. Solids containing a nitrate-to-$Cs_2ZnFe(CN)_6$ mole ratio of six reacted with a sharp explosion when heated to about 350 C while a mole ratio in the order of 0.4 appeared to be on the borderline. Laboratory observations demonstrated a lower tendency toward rapid reaction if the solids are dried and calcined rapidly.

In view of the effects of nitrate content in the $Cs_2ZnFe(CN)_6$ solids, it is recognized that additional process development is necessary to circumvent the potential hazards. Possible approaches to this problem include the following:

1. Chemical destruction of the nitrate ion.
2. Distillation of the nitrate as nitric acid.
3. Addition of inhibitors which, in themselves, introduce no hazards.
4. Extensive washing of the precipitate. An ionic material which will not be carried into the final product, such as ammonium carbonate, might be present in the wash solution to prevent peptization.

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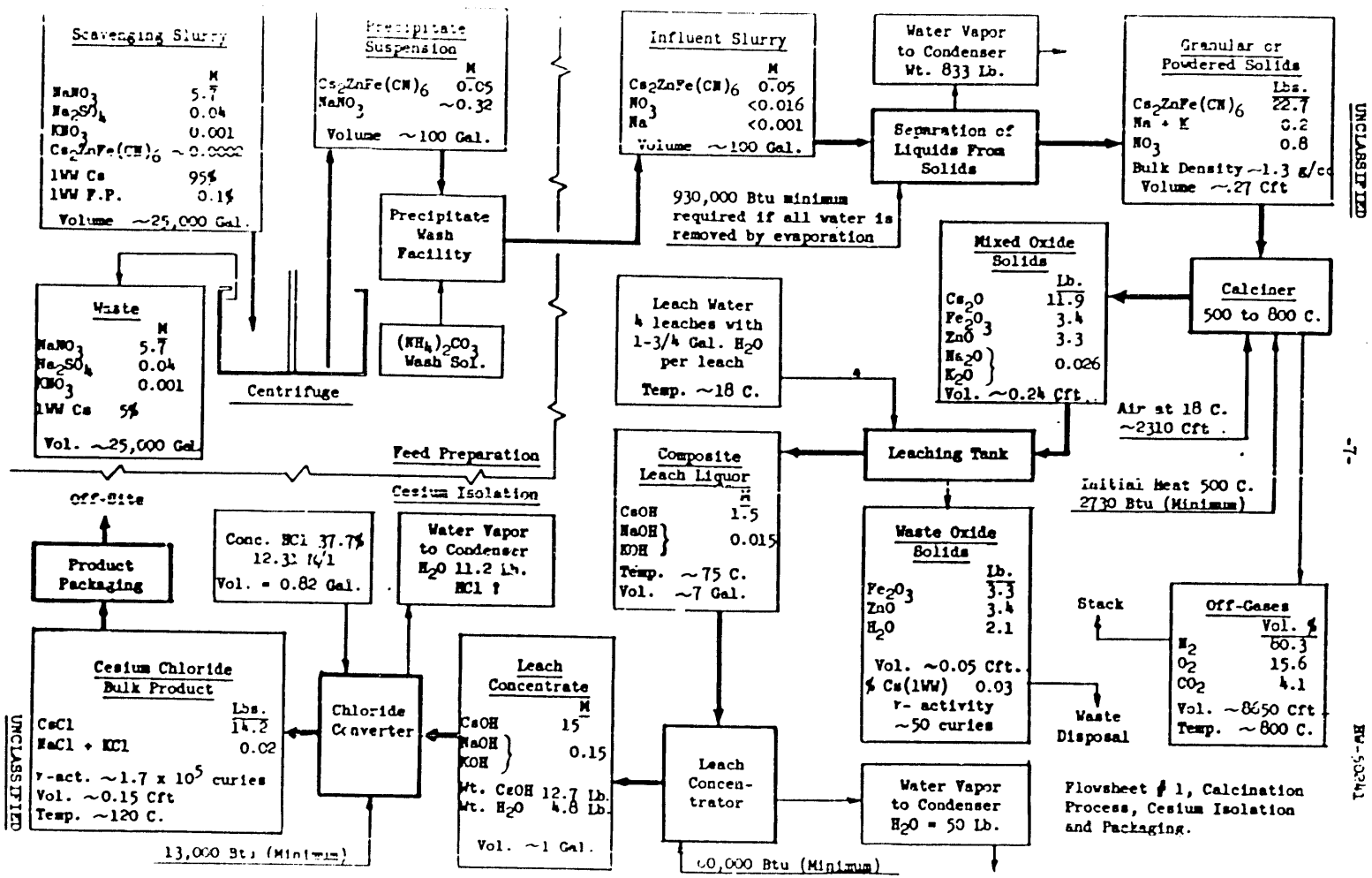

Flowsheet # 1, Calcination Process, Cesium Isolation and Packaging.

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