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# Effects of Changing Parameters on Chlorination Process of Rare Earth Metals and Actinides Mixture

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# Effects of Changing Parameters on Chlorination Process of Rare Earth Metals and Actinides Mixture

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## INTRODUCTION

Separation of actinides from rare earths has many applications, including nuclear materials extraction from minerals and nuclear fuel reprocessing [1]. This paper describes results of early stage study of a process for converting a rare earth and actinide metal mixture into an anhydrous chloride salt mixture for subsequent separation. It involves two steps: (1) hydrogenating of the metal by reaction with $H_2$, followed by (2) chlorination of the hydride by reaction with $Cl_2$. The first step is functional for reducing the particle size, thus minimizing mass transfer resistance for chlorination. An example of this process is a documented method for making $UCl_3$ from U metal involving reaction with $H_2$ followed by reaction with anhydrous HCl [2]. In this project, purification of cerium metal by removal of low concentration levels of U, Ga, Al, Fe, and Ta is being attempted via first conversion to chlorides. Because the maximum possible effectiveness of the separation is reliant on high efficiency conversion of metals to chlorides, the effects of changing various parameters, such as exposure time, chlorine concentration, operating temperature, and particle size, on conversion are reported in this paper.

## RESULTS

The metal samples were made by melting cerium as the base metal and mixing in aluminum, iron, gallium, tantalum, and uranium at 1000 ppm. This mixture was poured out into small coins approximately five grams in mass to be used in the hydrogenating step.

A chloride ion electrode (CIE) was used in order to determine the extent of chlorination. After chlorination, a small sample of about 100 mg is dissolved in water. After diluting this sample ten times and adding an ionic strength adjuster, the CIE is used to measure the concentration. This is then used to calculate the fraction of cerium hydride that was converted to cerium chloride. Effect of impurity metals on this analysis is neglected.

The system used includes a custom-built furnace and tube reactor with a frit insert for gas flow. The samples are held in a quartz basket with a frit in the bottom. This is held inside a glove box (Inert) under argon atmosphere. The thermocouple, pressure transducer, and mass flow controllers are controlled using National Instruments' modules and Labview software. Fig. 1 shows a flow diagram of this setup.

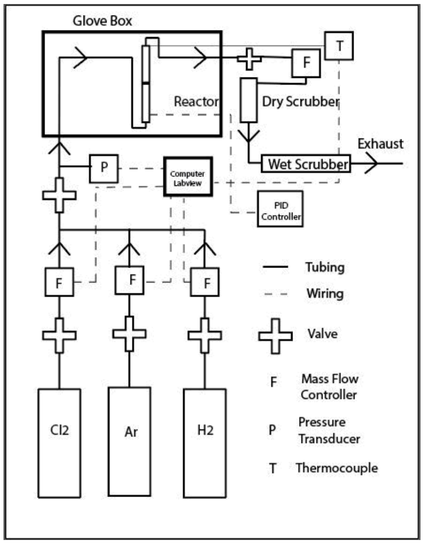

Fig. 1. Flow diagram of hydrogenating/chlorination setup.

Several experiments were run using 99.999% hydrogen gas at 100 cc/min and ramping the furnace up to 573 K at 5 K/min. It was found that hydrogenation was easily achieved over 99% after only 12 minutes and below 373 K. This step succeeds in shattering the metal buttons into many smaller particles (see Fig. 2).

Fig. 2. Cerium metal after hydrogenating step.

The first attempt at chlorination of cerium hydride was run at 573 K using 99.5% chlorine gas at 100 ccm for 30 minutes. This experiment achieved only 48.6% conversion to a chloride. It was also noticed that this reaction was very exothermic and raised the temperature over 100 K above the set point temperature.

The first parameter that was varied was exposure time. Several experiments were run at 573 K using 99.5%

chlorine gas at 100 cc/min for times between 10 to 33 minutes. Fig. 3 shows the maximum conversion (70%) to chloride for these tests was reached within about 15-20 minutes. It was visually apparent that the product had sintered/fused together into an agglomerated powder, shown in Fig. 4.

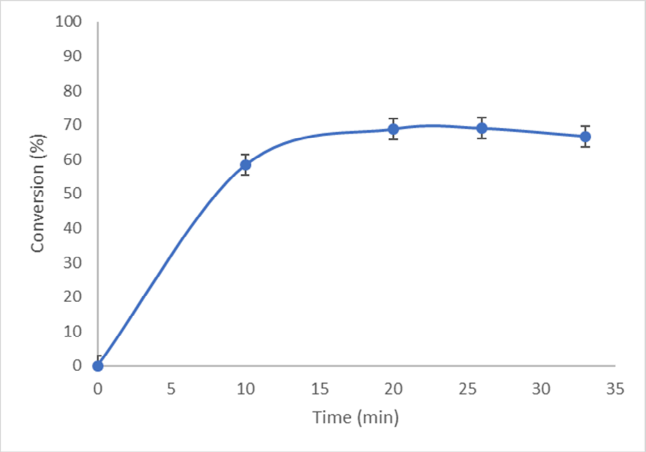

Fig. 3. Conversion of cerium hydride to chloride versus time at 573 K in 99.5% $Cl_2$ gas.

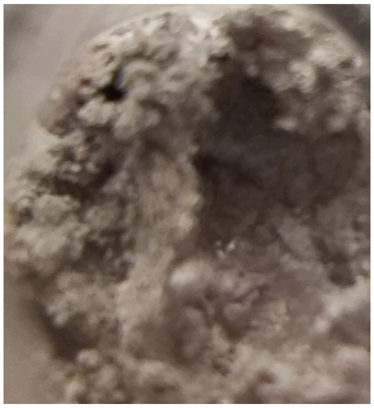

Fig. 4. Sintered cerium chloride after chlorination step.

The second parameter that was tested was $Cl_2$ concentration in the gas reactant. Hydride size may significantly affect the diffusion time of the chlorine gas through the particles. Several experiments were run at 573 K with 10% and 50% chlorine and hydride particles from 500 to 1000 µm and varied from 10 minutes to 11 hours. Fig. 5 shows the conversion versus moles of $Cl_2$ flowed through the reactor for all three $Cl_2$ concentrations. It can be seen that the conversion to chlorides increases with increasing $Cl_2$ concentration. This justifies the choice to use near pure $Cl_2$ gas and avoid dilution.

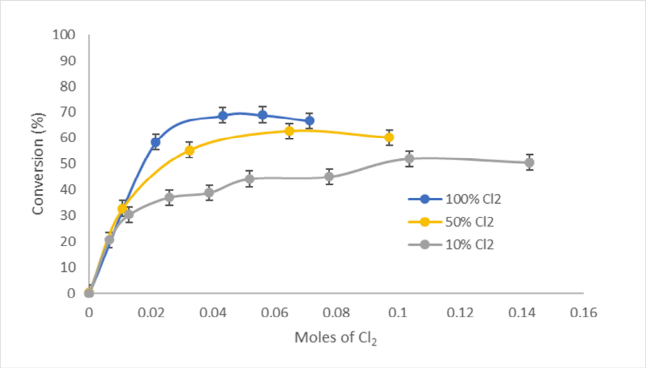

Fig. 5. Conversion versus moles of chlorine at varying concentrations.

The next parameter to be varied was temperature. These experiments were run using 99.5% chlorine and hydride particles 500 to 1000 µm at temperatures between 423 K to 523 K and varied from 10 to 90 minutes. Fig. 6 shows the conversion of these different temperatures. Best performance was recorded at 523 K. Comparable results were recorded for low cumulative flow of $Cl_2$ at 473 K, but those results appeared to be unstable or erroneous. It is an anomaly to observe degree of chlorination decrease with increasing cumulative flow of $Cl_2$.

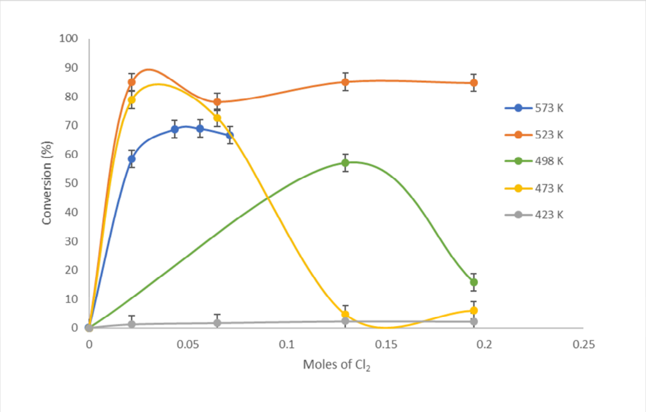

Fig. 6. Conversion versus moles of chlorine at varying temperatures.

The final parameter varied was hydride particle size. These experiments were run using 99.5% chlorine at 523 K and two sieves to obtain a maximum particle size 150 to 2000 µm for 60 minutes. Fig. 7 shows the conversion for the corresponding hydride particles for each sieve size. It can be seen that conversion decreases as hydride particle size increases. It was also observed that sintering occurred more as particle size decreased.

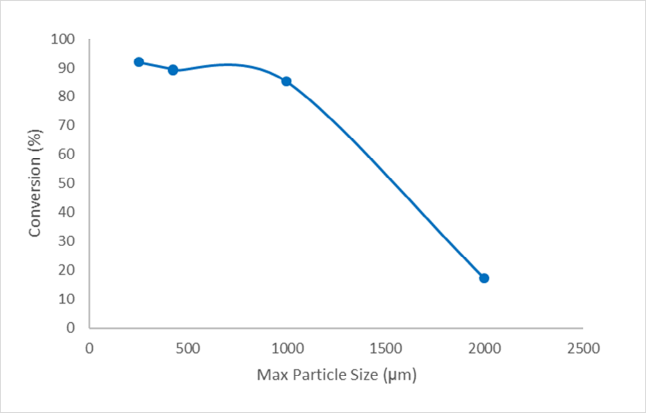

Fig. 7. Conversion versus max particle size.

In evaluating this result, we attempted to understand the data in terms of what may lead to inhibiting complete chlorination. The first observation made was that high temperatures lead to sintering which causes the chloride particle masses to fuse together. It is hypothesized that the hydride particles convert to chlorides from the outside first and follow the shrinking core model. If there is a sufficient amount of heat being generated and the temperature is high enough, such as with the experiments at 573 K, the chloride shell may fuse together and create an impermeable shell that the chlorine gas cannot diffuse through. This could explain the lower conversion at higher temperatures.

As a consequence of the above hypothesis, more sintering should produce lower conversion values, but this is not the case for the experiments run with varying particle sizes. This may be explained by another kind of sintering. The previous description is on a microscale and involves the shell of the particle sintering. Smaller particle sizes have less volume for the chlorine gas to diffuse through, thus increasing conversion. The heat generated still causes the chlorides to sinter, but on a macro scale where the particles fuse together.

The final question raised is the oscillation of high and low conversion for the experiments run at 473 and 498 K. As hydride materials are converted to chlorides, heat is being generated and promotes the conversion of other hydride materials nearby. These temperatures are at the upper limit of what will support optimal conversion.

In conclusion, this two-step process for converting actinide/rare earth metals to chlorides has been demonstrated up to 92% conversion. Smaller hydride particle sizes in the range of 150-250 µm and undiluted 99.5% chlorine gas works quickly enough at 523 K to be complete in 60 minutes.

## REFERENCES:

1. M.F. Simpson and J.D. Law; "Nuclear Fuel Reprocessing;" *Encyclopedia of Sustainable Science and Technology*, 2nd Edition, Springer, ed. R.A. Meyers, ISBN 978-1-4939-2493-6,
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