THE PRECIPITATION OF LARGE CERIUM CARBONATE BY Na_2CO_3 IN VARIOUS CONDITION AND ITS CHARACTERIZATION

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Abstract - **Cerium is one of the most abundant rare earth element. The application of cerium is mostly as catalysts for chemical processing, petroleum refining, catalytic converter, diesel additives and also can reduce emission of industrial gas released. The purpose of this study is to enlarge the size of cerium particle by precipitation method. Cerium carbonate was prepared using Sodium carbonate as precipitator. The effects of operational parameters to be studied were pH and concentration, while the other was fixed such as temperature at 50°C, stirring rate at 110 rpm, dosage rate, seed mass and effect of aging at 1 hours after completion of reagent addition. There are two methods of seeding precipitation been used to tested the different size of particle enlargement with pH and concentration as main parameter. High pH batch seeding precipitation shows the highest particle size at d (0.10), d (0.5) and d (0.9) which is 15.211, 47.605 and 91.748. Low concentration of Cerium carbonate gave the highest particle size in effect of concentration which was d (0.10) = 10.99 µm, d (0.5) = 41.87 µm and d (0.9) = 83.41 µm. The sample from Lynas Malaysia SDN BHD was taken as reference. It could be concluded that batch seeding precipitation method at high pH and low concentration shows great potential for enlargement of Cerium carbonate particle more than 40 µm.**

I. INTRODUCTION

Rare earth elements have a unique character because of particular electron configuration and are said to be the new material treasury due to their properties. Rare earth material has physicochemical characteristics that effect on its application. Formally, the major source of rare earth element is from weathered clay minerals formed through complex physical, chemical, and geobiological processes under natural conditions. The clay mineral act as an inorganic ion exchange resin onto which the hydrated rare earth elements absorb [6]. The ore was mining, the ore containing basnasites has high composition of cerium [7]. Bastnasite containing about 70% composition of rare earth element and 50% percent from it containing Cerium[13] .

In rare earth industry, controlling the physicochemical property index has become the key in industry development. The application effects of rare earth powder are determined directly according to its particle size. Many high-tech industries consume rare earth to be used in electronics, computers, clean energy processing, vehicle, health care and many others. [1].

Furthermore, particle size and distribution were very important performance indices for Cerium powder. Large particle of Cerium powder has extensive market application while fine powder has specific application. Normally, particle size and characteristic of powder was depended on temperature, pH, seed mass, effect of aging and reagent dosing rate [17]. Temperature with different annealing time also give a particle different sizes [16]. A supersaturation was control by stirred speed. According to Liu, high stirring speed increase the supersaturation. Therefore, suitable stirring rate was needed to prevent local supersaturation and helps mass transport process [4]. pH also effect the supersaturation level, which was influence particle size, size distribution and morphology of the precipitates [13]. If the feeding speed was very low, the rate of growth was larger than the rate of nucleation resulting in the growth of particles. If the feeding speed was fast, the rate of nucleation was larger than the rate of growth, resulting in generation of fine particles [4].

Hydrometallurgy method consist of digestion, leaching, precipitation and extraction [3]. The rare earth element can be dissolved with a solution by ion exchange process and the dissolved rare earth elements was recovered either by solvent extraction or precipitation method. Solvent extraction method was largely used on a commercial scale [14]. For precipitation formation, low solutes concentration is required to precipitate the rare earth from the solution. Each rare earth elements had a unique extraction steps and chemical processes and retention times. Sometimes, these elements require a reprocessing to achieve higher purity. After each element was extract, they are in form of carbonate which is can be dried, stored, and shipped. So high measure of precaution measure was needed to avoid environmental hazards [18]. To control the size of particle, agglomerate was a one of the methods. Agglomerate was an assembly of particles rigidly joined together as by partial fusion, sintering or growing together. The agglomeration was a processed that occur in crystal nucleation grow [15].

Cerium Carbonate was prepared by precipitation of Sodium carbonate and Cerium chloride. It is difficult to get successful scale up particle size due to the absence of validated method. Particle size and morphology of rare earth elements are depended on pH, temperature, seed mass, effect of aging and reagent dosing rate [4]. So, in this article, our objective is to increase the size of a Cerium carbonate particle by precipitation with Sodium carbonate. The parameter we observe was pH, how the pH will affect the size of the particle. Hence, two methods of seeding precipitation were tested in order to enlarge the size of Cerium carbonate particle.

The size of Cerium carbonate at d (0.5) is expected to be more than 40 micrometer. Furthermore, characterization and morphology of Cerium Carbonate powder were analysed by Malvern particle size analyzer.

II. METHODOLOGY

A. *Materials and Apparatus*

The material used are Cerium(III) chloride ($CeCl_3$) and sodium carbonate (Na_2CO_3). The apparatus used are hot stirrer plate and pH Meter. The hot stirrer plate will supply heat to the desired temperature of solution while stirring. The dosage flow rate of the $CeCl_3$ and Na_2CO_3 is controlled using Cole-Palmer Masterflex® L/S® Precision Variable-Speed. The pH meter is a scientific instrument to measure hydrogen ion activity and water based solution, to indicate whether the solution is acidity or alkalinity.

B. Rare Earth Oxide (Concentration of Cerium Chloride)

Rare earth oxide (REO) content in the $CeCl_3$ was the same as molarity. It was checked before starting the precipitation. 0.05 g of L-Ascorbic Acid was put into 250 mL conical flask and dissolved with 50 mL of distilled water. 1mL of CeCl3 was pipette using Cole-Parmer EX Adjustable Volume Pipette, 4-5 drop of Methyl Orange, 4-5 drop of Ammonia, 10mL of Hexosaminidase A (alpha polypeptide) know as HEXA and 4-5 drop of Xylene Orange. The solution was titrated with Ethylenediaminetetraacetic acid (EDTA) until magenta solution turn to orange solution. The amount of volume EDTA use was multiply by mol of EDTA to get the value of REO.

C. Method of addition seed

1. Seeding precipitation

For normal seeding precipitation, 500mL of 1.29 M $CeCl_3$ and 500 mL of 0.75 M Na_2CO_3 were prepared for precipitation. 450mL water was filled into 3 L beaker, then added 150mL of $CeCl_3$. The solution was heated to 50ºC and agitate at 110rpm speed using hot magnetic stirrer. 2.5g of ($Ce_2(CO_3)_3$ seed from Lynas sample was added into the solution and stirred for 5 minutes. Then Na_2CO_3 and $CeCl_3$ was dosed parallel, with dose rate of 1.5 mL/min and 1.0 ml/min consecutively as shown in Figure 1. The sample was taken at pH 5.2 and 5.8 to observe the particle size at different pH. The precipitation process was stop at pH 5.85. Both sample was left for one hour in room condition for aging.

2. Step-wise precipitation

For step-wise seeding precipitation, 2.5 g of ($Ce_2(CO_3)_3$ from Lynas sample was used as seed. The seed was separated into 0.5 g each and slurry with 50 mL distilled water for step-wise seeding preparation and put into a labelled bottle. 500mL of 1.29 M $CeCl_3$ and 500 mL of 0.75 M Na_2CO_3 were prepared for precipitation. 200mL of water was added into 3 L beaker and then add 150 mL of CeCl3. The solution was heated to 50ºC and agitate at 110 rpm speed. First bottle of seed was added into the solution and stirred for 5 minutes. Then Na_2CO_3 and $CeCl_3$ was dosed parallel, with dose rate of 1.5 mL/min and 1.0 ml/min consecutively. After 70 minutes, when pH and concentration was constant, second bottle seed was added into the beaker. Every 60 minutes, seed was added into the beaker and stop at the fifth bottle seed. The sample was taken at pH 5.2 and 5.8. Both sample was left for one hour in room condition for aging. The precipitation process was stop at pH 5.85.

D. Effect of $CeCl_3$ concentration

10 ml of 1.29 M $CeCl_3$ was diluted with 50 ml of water in 250 ml beaker. 0.75 M of Sodium carbonate was prepared by dissolving about 40 g of Na_2CO_3 into 500 ml of distilled water. The solution was stirred at 110 rpm and temperature of 60ºC for about 5 minute. Then about 1 g of solid $Ce_2(CO_3)_3$ was put into the beaker as a seed and stirred for 5 minute. Then $CeCl_3$ and Na_2CO_3 was dosed parallel into the beaker. The dosage rate is controlled by using two burette which one contained 1.29 M $CeCl_3$ and the other was 0.75 M of Na_2CO_3 as shown in Figure 1. Both $CeCl_3$ and Na_2CO_3 were release drop by drop. 100 ml of $CeCl_3$ is precipitate with Na_2CO_3 until pH 5.45. After pH 5.45, the solution was left for one hour in room condition for aging purpose. The experiment was repeated by using 60 ml, 70 ml, 80 ml and 90 ml of distilled water to dilute 10 ml of 1.29 M $CeCl_3$.

E. Particle analyze of Cerium carbonate by Malvern

The particle size of Cerium carbonate was analyzed by using Malvern particle size analyser. The refractive index for Cerium carbonate was 1.8 and the pump speed was set at 2300 rpm. The dispersant use was distilled water.

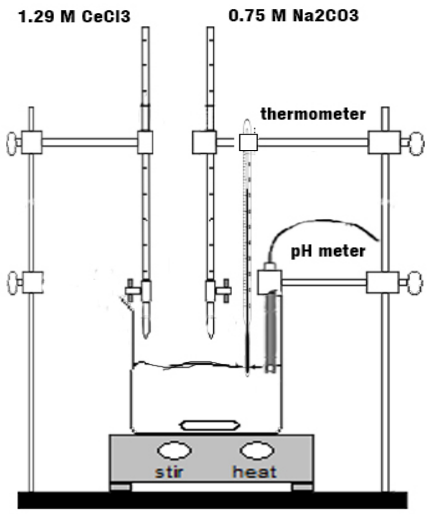

Figure 1: Apparatus set up for parallel precipitation both for Normal and Batch precipitation

RESULTS AND DISCUSSION

A. The differences of particle between seeding and step-wise precipitation

Particle size differences between the particle was compared. Figure 2, it shows a comparison between the particle size of normal seeding and step-wise precipitation. The mean frequency and standard deviation was plotted. The diamond plot show the step-wise and square plot show the seeding. From the Figure 4.1. In the step-wise, base and seed was added frequently to control the supersaturation. In this study, low supersaturation reaction was occurred when it taken 5 to 6 hours to complete the reaction by titration of dosage flowrate 1.0 ml/min for $CeCl_3$ and 1.5 ml/min for Na_2CO_3. With the low supersaturation control, the particle grows larger [20]. Sudden increase in supersaturation will cause large number nuclei to form. If the nucleation formation was high then growth rate, many nuclei will form but will grow very little [9] According to Demopoulos, the controlled addition of seed as a means of controlling supersaturation has been successfully demonstrated in the case of high grade of others particle. The particle size for supersaturation control at d (0.1) = 13.41 µm, d (0.5) = 41.17 µm and d (0.9) = 79.19 µm. In the normal seeding precipitation, one time of seed addition to the solution will make the seed size distribution was so coarse that reduced seed specific surface area leads to lowered active centers and increased probability of nucleation explosions[2]. The nucleation explosion will increase the fine particle content rapidly, therefore give small particle size. The particle size for seeding precipitation at d(0.1) = 8.39 µm, d(0.5) = 37.92 µm and d(0.9) = 78.89 µm.

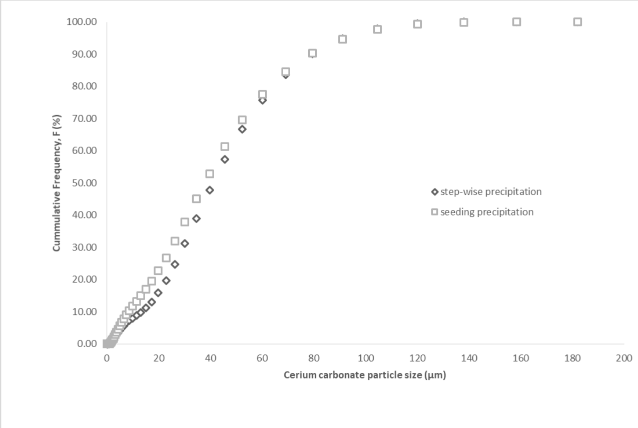

Figure 2: Particle size of Cerium carbonate particle comparison between step-wise and seeding precipitation.

B. The effects of $CeCl_3$ concentration on particle size

The effect of concentration on the particle size of Cerium carbonate was shown in Figure 4.2. The concentration of $CeCl_3$ played an important role in determining the particle size of Ce_2CO_3. In this study various concentration of $CeCl_3$ were used to determine the particle size. The different in solution concentration will give different peak for particle size distribution [8]. The lower concentration gave large particle size and wide distribution curves [9]. Low concentration of solution gave instability and recrystallization to occur give the particle larger in size [10]. While the high concentration effects the final size of the stabilizes new developed surface during homogenation and production of smaller particle [10]. The direct growth of particle size of Ce_2CO_3 will increase with increasing surface in contact and if the newly developed surfaces are not stabilized due to low concentration [12]. Stabilization serves to protect colloids from aggregation or phase separation. Aggregate consist of two or more primary particle that bound together by rigid chemical bonding that resulted from sintering or cementation [20]. The two main mechanisms for colloid stabilization involve steric and electrostatic modifications. Electrostatic stabilization is based on the mutual repulsion of like electrical charges. By altering the surface chemistry to induce a charge on the surface of particles it is possible to enhance the stability of the colloidal dispersion. From the study, the 0.14M shows particle size of d (0.10), d (0.5) and d (0.9) which is 8.83 µm, 42.95 µm and 86.45 µm.

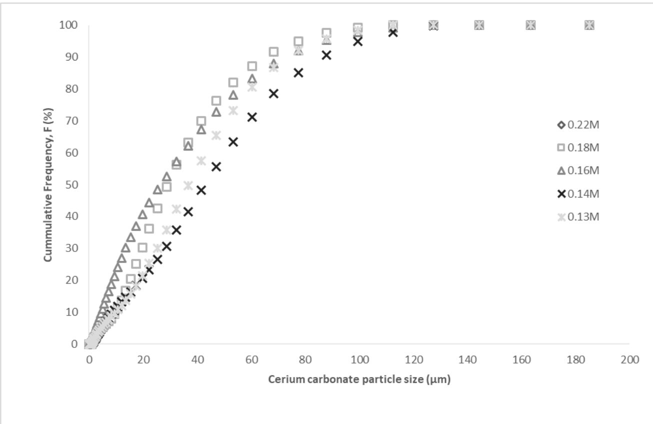

Figure 3: Particle size of Cerium carbonate particle comparison effect by concentration

III. Conclusion

The operational factor as addition of seed and $CeCl_3$ concentration had an important effect on particle size. The Cerium carbonate was prepared by adding Sodium carbonate as precipitator. Under step-wise precipitation, Cerium carbonate particle size was more than 40 µm which was at d (0.5) = 41.17 µm. The 0.14M $CeCl_3$ concentration particle size d (0.5) 42.95 µm. It could be concluded that step-wise precipitation and 0.14 M $CeCl_3$ concentration shows a great potential for enlargement of Cerium carbonate particle more than 40 µm.

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