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Sintering of Hydroxyapatite at Extra Ordinary Low Temperature of <200^{O}C- A Way Forward to the Effective Immobilization of Radioiodine

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1. Introduction

Used nuclear fuel reprocessing industry is somehow suffering a number of challenges in order to fully establish its worth in the nuclear industry. The establishment and licensing of the used nuclear fuel reprocessing facility may require the facility to adopt efficient methods to capture and immobilize the volatile radionuclides expected to be evolved in the off-gas system[1]. Handling and immobilization of ILW volatile fission by-products like I-129, one with a very long half-life of ~1.6 x 10^7 years, require more attention. In efforts to develop appropriate options for iodine waste, Hydroxyapatite (HAP) has been identified as a suitable candidate. The suitability of apatite for its use as solid matrix for long-term disposal of I-129 is because of its ability to accommodate iodine ions having an ionic radius of 196 pm at channels within its crystal structure as well as its good resistance against radioparagenesis[2], a process of matrices degradation due to radioactive decay of the incorporated material[3]. In this regard iodide substituted and iodate replaced calcium hydroxyapatite has already been synthesized and reported elsewhere[4,5].

In case of retaining the maximum quantity of loaded contents of the volatile radioisotopes like radioiodine, the sintering temperatures need to be lesser than their volatilization temperatures (<500^{O}C). In this case the vitrification route and other consolidation techniques could not assure the retention of radioiodine within the sintered body and therefore efforts are being made to sinter different formulations of apatite at temperatures as low as 300^{O}C in order to retain maximum quantities of loaded radioiodine within the apatite structure[5].

In this study we have successfully sintered the synthesized HAP at an extraordinary low temperature of <200 ^{O}C by using the technique of cold sintering[6] as the first attempt. In this effort we have got 87% relative dense sintered pellet at a temperature of 180^{O}C under a uniaxial pressure of 300MPa.

2. Methods and Results

2.1 Apatite Synthesis

Initially the crystalline apatite has been synthesized by using the wet precipitation method as described elsewhere[7]. Two solutions, A & B, were prepared by dissolving each di-ammonium hydrogen phosphate $\{(NH_4)_2HPO_4\}$ and calcium nitrate $\{Ca(NO_3)_2{\cdot}_4H_2O\}$ in 100ml of double deionized water respectively. The pH of the solutions was adjusted at 10.5 by using concentrated ammonia $\{NH_4(OH)_2\}$. All used materials were of reagent grade. Then solution "A" was mixed with solution "B" dropwise during one hour under continuous stirring at the rate of 150RPM and temperature was maintained at 35^{O}C. The pH of the solution was continuously monitored by using digital pH meter and was maintained at 10.5 throughout the synthesis period by the dropwise addition of concentrated ammonia. At the end of synthesis, precipitates were left inside the parent solution for 10 hrs under continuous stirring at 35^{O}C for ageing. After 10hrs, the suspension was filtered and thoroughly washed with double deionized water. Finally the filtrate was freeze dried at a temperature of -80^{O}C.

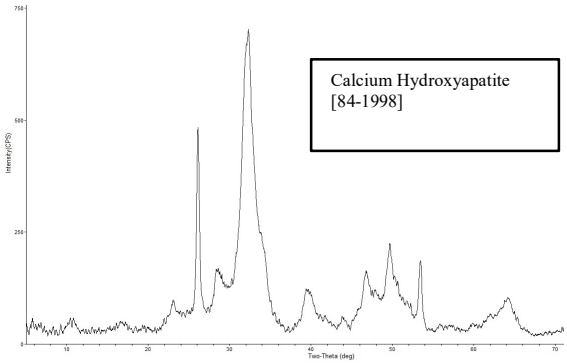

Fig. 1. XRD patterns of calcium hydroxyapatite synthesized at 35^{O}C.

2.2 Powder Characterization

XRD pattern of the apatite powder was obtained by using SmartLab, RIGAKU, high resolution powder X-ray diffractometer and the 2Θ range was between 10 and 70◦ (Fig.1.). Archimedes method as well as helium pycnometer were used to measure the density of the sintered pellet. SEM of the sintered sample was carried out to see the porosity and microstructure (Fig. 2.).

2.3 Cold Sintering of Apatite

The sintering of apatite powder by using cold sintering technique has been investigated first time in order to extend the use of this technique for the extra ordinary low temperature of <200 ^{O}C sintering of iodate substituted HAP as upcoming plan. 1 g of apatite powder was mixed with 10 wt% of deionized water by using pestle and mortar. The powder was then poured in a steel mold and uniaxial pressed under the pressure of 300MPa for 3hrs. In order to provide controlled heating during the pressing, heating tape was wrapped around the steel mold. The pressing time was divided into three steps.

Step-I
Pressing at room temperature for 10 minutes
Step-II
Pressing with heating (25^{O}C to 180^{O}C) for 120 minutes
Step-II
Pressing during cooling for 50 minutes

After 3 hrs, pressure was released and a sintered/dense pellet of the apatite was obtained. The relative density of 87% was achieved as measured by using the pycnometer whereas theoretical density of the apatite was used as 3.16 g/cm^3.

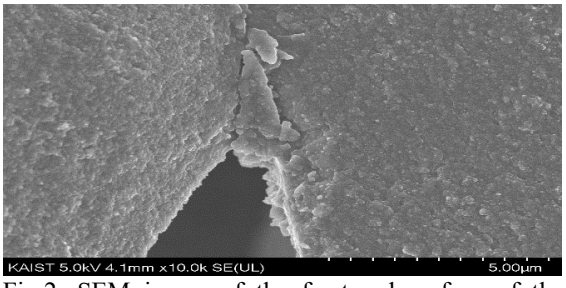

Fig.2. SEM image of the fractured surface of the sample sintered at temperature <200^{O}C.

3. Conclusion

In this work, ultralow temperature sintering of apatite by using cold sintering technique was demonstrated. This leads to our final goal of development of an ultralow temperature sintered matrices for the immobilization of I-129 for long term geological disposal.

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