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# Cold Sintering of Iodate Substituted Calcium Hydroxyapatite and its Durability Testing

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## 1. Introduction

Volatile radionuclides present in the radioactive waste stream of the used nuclear fuel reprocessing facilities are one of the major causes of environmental hazards. Among these radionuclides radioiodine is most important because of its very long half-life and high mobility. Therefore, effective adsorption and immobilization of radioiodine are required to protect the environment from its harmful effects. Radioiodine has low volatilization temperature of 500ºC and therefore cannot be retained in immobilization matrix treated at high temperature (e.g. vitrification, HIP etc.)

Calcium Hydroxyapatite has shown a loading capacity of iodine up to 10wt% in its crystal structure. This loading can be achieved by the substitution of iodine in the form of iodide or iodate with the hydroxyl group of the apatite [1, 2]. However, sintering of the synthesized substituted calcium hydroxyapatite is required to increase the density and to produce a compact matrix which has either been carried out at high temperatures (>800ºC) or sophisticated sintering techniques (HIP, SPS etc.) have been applied [3].

In this study, for the first time we have sintered the synthesized, dried iodate substituted calcium hydroxyapatite (IO-HA) in single step sintering without the use of any binder or additive. The sintering temperature of 200°C, 500 MPa uniaxial pressure and 10 minutes holding time have been optimized to achieve sintered relative densities ≥ 95%. The sintered matrix was then subjected to product consistency test (PCT) to test its chemical durability.

## 2. Methods and Results

### *2.1 IO-HA Synthesis*

Wet precipitation method as described in reference [3] has been used to synthesize crystalline iodate substituted calcium hydroxyapatite. The pH of the precursor solutions and reaction were adjusted at 10.5 by using concentrated ammonia. Then anionic solution was mixed with cationic solution dropwise during 60 minutes under continuous stirring at the rate of 200RPM and temperature was maintained at 70°C. At the end of synthesis, the precipitate was left inside the parent solution for 12 hrs at 30°C for ageing. After 12hrs, the suspension was filtered and thoroughly washed with double deionized water. Finally the filtrate was dried overnight at a temperature of 110°C by using a vacuum oven.

### *2.2 Powder Characterization*

XRD pattern of the synthesized powder was obtained by using SmartLab, RIGAKU, high resolution powder X-ray diffractometer and the $2\Theta$ range was between 20 and 60° (Fig.1.).

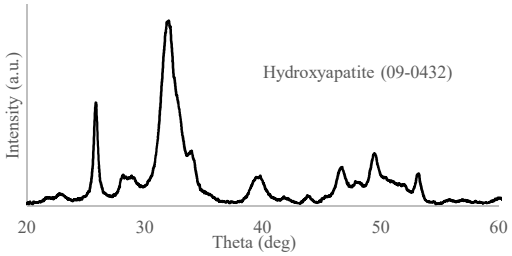


Fig. 1. XRD patterns of the IO-HA showing no other phase except apatite.

FTIR of the IO-HA revealed the presence of small amounts of carbonates as the synthesis was carried out in an air environment. All other vibrations were related to the apatite functional groups (Fig.2.).

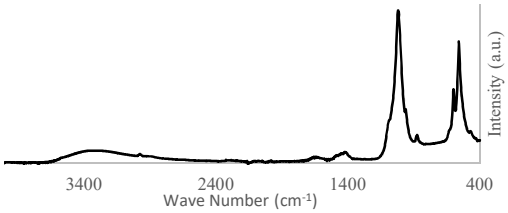


Fig. 2. FTIR spectra of the synthesized IO-HA.

Iodate quantification was carried out by using inductively coupled plasma-optical emission spectroscopy (ICP-OES) of the solution before and after the completion of the reaction. The surface area

of dried powder was measured as 112.35 $m^2/g$ by using the BET method. The bulk density of dried powder was measured by using helium pycnometer and was 2.70 $g/cm^3$.

Raman spectroscopy of the samples was carried out before and after PCT to confirm the iodate environment (Fig. 3).

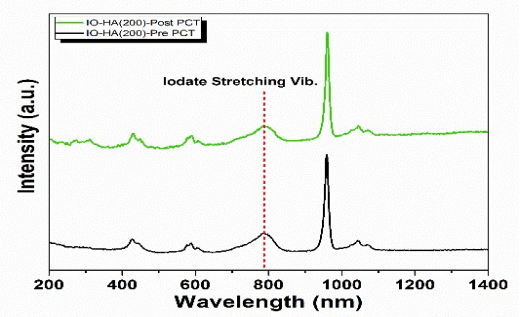


Fig. 3. Comparative Raman spectroscopy of the sintered IO-HA before (black) and after (green) PCT.

### *2.3 Sintering of Iodate Substituted Calcium hydroxyapatite*

The sintering of IO-HA powder was carried out by using a uniaxial press. 1.20 gm of dried powder was poured into steel mold having10 mm internal diameter. The mold was covered with a heating band and placed in the uniaxial press. Pre-optimized uniaxial pressure (500 MPa), temperature (200°C) and holding time (10 minutes) was applied to sinter the IO-HA.

### *2.4 Vickers Hardness*

The hardness of sintered samples was measured by using the Vickers testing procedure. The load of 200 g.f was applied for a dwell time of 10 sec. An average value of 2 GPa of Vickers hardness was measured whereas the yield strength was calculated as 0.80 GPa.

### *2.5 Compressive Strength*

Compressive strength is an important parameter for the qualification of an immobilization waste matrix. A value of 3.45 MPa has been set as the minimum requirement for the cement-based matrix. 200°C sintered IO-HA has exhibited exceptional compressive strength of 170 MPa which is many folds of the regulatory requirements set by NRC and Russian regulatory bodies.

### *2.6 Product Consistency Test (PCT)*

Product consistency test of the sintered matrix was carried to as per American Society of Testing Materials (ASTM) standard-ASTM C1285-02. The normalized leaching rates of constituent elements of the matrix are given in the table-1 and are better than the cement-based waste forms.

**Table-1.** Normalized leach rate indexes (NLRi) of elements of the low temperature sintered IO-HA matrix based on PCT.

| | Ca | P | I |
|---|---|---|---|
| NLRi ($g.\ m^{-2}.d^{-1}$) | $7 \times 10^{-7}$ | $3 \times 10^{-7}$ | $2 \times 10^{-5}$ |

## 3. Conclusion

In this work, single step, low temperature sintering of apatite by using dried powder without any additive was demonstrated first time. We have optimized sintering conditions to achieve the highest relative density as well as good mechanical properties. The sintered matrix has shown good chemical durability and has been qualified by the PCT test. Thus, the developed low temperature sintering technique stands out as an appropriate method for the development of stable, efficient and economical waste matrix for the immobilization of I-129 for long-term geological disposal.

## Acknowledgment

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## REFERENCES

[1] P. Alberius Henning, S. Lidin, and V. Petříček, “Iodo-oxyapatite, the first example from a new class of modulated apatites,” *Acta Crystallogr. Sect. B Struct. Sci.*, vol. 55, no. 2, pp. 165–169, Apr. 1999.

[2] A. Coulon *et al.*, “Key parameters for spark plasma sintering of wet-precipated iodate-substituted hydroxyapatite,” *J. Eur. Ceram. Soc.*, vol. 36, no. 8, pp. 2009–2016, 2016.

[3] L. Campayo, A. Grandjean, A. Coulon, R. Delorme, D. Vantelon, and D. Laurencin, “Incorporation of iodates into hydroxyapatites: a new approach for the confinement of radioactive iodine,” *J. Mater. Chem.*, vol. 21, no. 44, p. 17609, 2011.