

Apatite Based Ceramic Waste Forms for Immobilization of Radioactive Iodine, An Overview - 16155

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ABSTRACT

Apatite based ceramic waste forms are the most promising candidates for immobilization of radioactive iodine (I-129). While lead-vanadium based apatites have been studied for a long time, significant progress has been made in recent years in the domain of calcium-phosphate based apatites for iodine immobilization. This article is an attempt to present an overview of the progress that has been made in terms of developing novel synthesis and processing routes to contain iodine in apatite based ceramic waste forms. The challenges associated with current state-of-the art waste form synthesis techniques along with novel routes to synthesize these waste forms at low temperatures have also been discussed.

INTRODUCTION

One of the key components to a feasible and sustainable nuclear fuel cycle is a viable set of waste forms for the radionuclides and fission products. Of particular concern are the highly volatile radionuclides, e.g., H-3, Tc-99, I-129, Cs-137. In particular, the long half-life of I-129 ($\sim 1.6 \times 10^7$ years) combined with its high solubility in water (in anionic state) and its technical challenges associated with its capture in conventional radioactive waste forms (glasses or cements) pose serious concerns for its geological disposal.[1] The current proposed technology for the removal of iodine from reprocessing plant off-gas is to pass it through Ag-exchanged zeolite (AgZ) to form chemisorbed AgI.[2] Since silver is an RCRA metal, iodine is typically extracted from AgZ and further processed for immobilization into a durable waste form. Iodine is not amenable to conventional borosilicate vitrification routes because of its low solubility in some glass chemistries, but more importantly due to its high volatility at typical glass processing temperatures (1000–1100°C).[3] Therefore, considerable effort is being made to develop alternative waste forms for iodine. However, most proposed waste forms to date have not achieved sufficient maturity and satisfactory properties (specifically: ease of processing, high waste loading, and high chemical durability) to be considered as promising technologies. This article presents an overview of the current state of research pertaining to the development of apatite based ceramic waste forms for the immobilization of radioactive iodine.

JUSTIFICATION FOR THE USE OF APATITES

Apatites have long been considered as a potential waste form for the immobilization of iodine isotopes. Due to their unique channel structure, it is easily

amenable to the incorporation of a wide range of fission products, including halides, into its crystal structure.[4] In addition, it has also been suggested that apatites have acceptable durability against radiation.[5, 6] The challenge, however, lies in the large ionic radius of the iodide ion. Considering the large ionic radius of iodide (I^- , 196 pm), it is difficult to find any naturally existing iodine containing apatites, thus leading to a scarce amount of knowledge and basic understanding about iodo-apatites.[4] Due to these reasons, most of the iodine containing apatites produced so far have had several shortcomings that have not allowed them to be adopted for iodine immobilization. The shortcomings may be issues, such as low waste (iodine) loading, poor chemical durability, or inability to scale up production. Progress is being made in the development of apatites for iodine immobilization, but in order to find the solution to the problem, one must thoroughly investigate the problem and understand the work that has led to the current state of apatite research within the scientific community.

Early Iodo-Apatites

Early on, iodine-containing apatites were synthesized by various researchers for various purposes. None of those, however, aimed at developing a waste form for immobilization of radioactive iodine. It began as early as 1959 when Merker and Wondratschek were studying lead apatites.[7] It was not, until about four decades later, however, when the topic of iodine immobilization in apatites was brought to light by Audubert et al.[8] Within that timeframe, there were only a few other investigations into iodo-apatites. Sudarsanan et al. synthesized cadmium vanadate iodide apatite from the melt of cadmium vanadate and cadmium iodide. [9, 10] It was concluded that due to a short c-dimension, there were deficiencies in the halide content and, as a result, modifications in the typical apatite structure occurred. This led to the formation of vacancies in the Cd(2) position (which formulates the apatite channel) in order to maintain charge balance. Apart from that, the only other iodo-apatite studies that were reported in this timeframe involved the use of pyramidal perrhenates (ReO_5).[11, 12] This is a step away from the standard structural and chemical moieties, which comprise of a tetrahedral MO_4 structure. For example, Baud et al. made an attempt to synthesize barium perrhenate iodide ($Ba_{10}(ReO_5)_6I_2$) *via* solid state route.[11] However, the as synthesized apatite mineral had the composition $Ba_{10}(ReO_5)_6I_{0.77}(OH)_{1.23}$, depicting uptake of moisture during synthesis. It was concluded that due to the electrostatic repulsion of the oxygen atoms of the pyramidal perrhenates on the IBa_6 octahedra that hydroxyl ions began to substitute for the halogen within the channel. In another study, Schriewer and Jeitschko, made an attempt to synthesize strontium perrhenate iodide apatite ($Sr_{10}(ReO_5)_6I_2$) *via* solid state route.[12] Although we could not find any information about the experimental chemical composition of the apatite formed in this study, it is interesting to note that the as synthesized iodo-apatite had an orthorhombic crystal structure, whereas the majority of iodo-apatites have hexagonal crystal structure.

Calcium-Phosphate Iodo-Apatites

One of the most commonly-known apatites within the scientific community is hydroxyapatite, which has a chemical formula, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Owing to the ability of hydroxyapatite to accommodate halide ions (F^- , Cl^- , Br^-) in its crystal structure, attempts have also been made to incorporate iodide (I^-) for the hydroxyl (OH^-) ion within the apatite channel. However, success in this direction is still eluding the scientists. The only study that has reported on successful substitution of $\text{I}^- \leftrightarrow \text{OH}^-$ in $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ using wet chemical synthesis has been published by Phebe and Narasaraju.[13] However, their assertions were highly preliminary in nature and it has been difficult to reproduce those results by any other researcher worldwide.[14] The successful attempts to incorporate iodine into calcium phosphate apatites utilized iodate (IO_3^-) instead of iodide (I^-) as the precursor for iodine, resulting in a solid solution with the general formula, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-x}(\text{IO}_3)_x$. The first successful attempt was made by Henning et al. where they synthesized a superstructure of an apatite material with the chemical formula, $\text{Ca}_{15}(\text{PO}_4)_9\text{IO}_3$ using a flux method.[15] However, considering that the material was synthesized at high temperature (850 °C) and under highly controlled conditions, it was difficult to consider this technique for waste form development. Recently, Campayo et al. synthesized a calcium phosphate iodate apatite with experimental composition $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{1.6}(\text{IO}_3)_{0.4}$ using low temperature wet chemical synthesis aimed at immobilizing iodine.[16] Although halide containing apatites (for example, fluorapatite) are known for their high chemical durability in neutral and basic environments, the structural analysis of iodate-containing hydroxyapatite revealed the lack of local order around the iodate ions as these ions do not cluster around the apatite channels, something that is not typically observed in apatites.[17] This raises concerns about the long term chemical durability of this waste form. Increasing iodine waste loading in these apatites is another crucial aspect that needs to be addressed in the near future.

Lead-Vanadate Iodo-Apatites

Lead-vanadate apatite [$\text{Pb}_{10}(\text{VO}_4)_6\text{I}_2$] has been extensively studied as a potential waste form for iodine immobilization. Due to the fact that lead and vanadium have larger ionic radii than calcium and phosphorous, lead-vanadate apatites are capable of incorporating iodine into its structure. Due to this, many variations on the synthesis of lead-vanadate iodide apatite have been explored over the years. Lead vanadate iodide was first synthesized by Merker and Wondratschek by melting lead vanadate and lead iodide in a vacuum sealed vessel in the temperature range of 500-800°C, while the crystallographic data on these minerals was obtained by Audubert et al.[7, 18] Further, Audubert et al. synthesized lead vanadate iodide, $\text{Pb}_{10}(\text{VO}_4)_6\text{I}_2$ within a matrix *via* solid state sintering by compacting a lead iodide core within the center of an outer layer of lead vanadate and consolidating the green body at 700 °C and 25 MPa.[8] Other high temperature synthesis methods include (i) mixing stoichiometric amounts of the precursors (PbO , PbI_2 , V_2O_5) corresponding to $\text{Pb}_{10}(\text{VO}_4)_6\text{I}_2$, and heating them

in a sealed quartz ampoule at 700 °C for 5 h under 35 MPa pressure, or (ii) hot isostatic pressing at 700°C for 2 h under the pressure of 200 MPa.[19, 20]

Although various solid state synthesis routes have yielded the desired Pb-V-I apatite, the major drawback with these synthesis routes is the need for a higher processing temperature. Iodine typically volatilizes at a temperature >500 °C and, as a result, the majority of the synthesis techniques investigated so far have been confined to sealed vessels and highly controlled environments. This problem is further aggravated by the poor chemical durability of stoichiometric $\text{Pb}_{10}(\text{VO}_4)_6\text{I}_2$ which demonstrates a leach rate (in pure boiling water) that is two orders of magnitude higher than for silver iodide-embedded glass waste forms.[19] This has resulted in a significant research effort focused on developing low temperature synthesis routes and improving the chemical durability of Pb-V-I based apatites. In this pursuit, it was observed that partial substitution of $(\text{VO}_4)^{3-}$ by $(\text{PO}_4)^{3-}$ in the apatite structure, resulting in a mineral with chemical composition $\text{Pb}_{10}(\text{VO}_4)_{4.8}(\text{PO}_4)_{1.2}\text{I}_2$, not only lowered the densification temperature of the ceramic body from 700 °C to 540°C (25 MPa), but also had a significant increase in the densification of the powder compact, thus increasing its chemical durability (due to a decrease in surface area).[21] This development resulted in a flurry of studies involving synthesis of Pb-V-P-I based apatites using various other techniques including spark plasma sintering,[22, 23] microwave dielectric heating,[24] and high energy ball milling.[25] The research in this direction currently still continues to be explored.

Future research on iodine containing apatites

As discussed above, most of the research on iodine immobilization in apatites has focused either on Pb-V-I or Ca-P-I system. However, there are several other systems that have demonstrated their ability to incorporate iodine in their crystal structure. For instance, cadmium vanadate iodide ($\text{Cd}_{10}(\text{VO}_4)_6\text{I}_2$), barium rhenium perrhenate iodide ($\text{Ba}_{10}(\text{ReO}_5)_6\text{I}_2$) and strontium rhenium perrhenate iodide ($\text{Sr}_{10}(\text{ReO}_5)_6\text{I}_2$), are potential candidate waste forms for iodine immobilization.[9, 11, 12] According to a recent computational study on the structure of iodine containing apatites with general formula $\text{A}_5(\text{XO}_4)_3\text{I}$, the A-site cation is capable of holding either Ag^+ , K^+ , Sr^{2+} , Pb^{2+} , Ba^{2+} and Cs^+ , whereas the X-site cation can hold Mn^{5+} , As^{5+} , Cr^{5+} , V^{5+} , Mo^{5+} , Si^{4+} , Ge^{4+} and Re^{7+} depending on the overall chemistry of the system.[26] Therefore, there is enough scope to design chemically durable apatite based waste forms for immobilization of radioactive iodine.

Another area that needs significant research effort in this field is to develop low temperature synthesis methods where these minerals can be produced under ambient conditions. This will not only lower the overall cost of waste form development, but will also allow the integration of a production scale-up. One such example is aqueous processing (for example, co-precipitation technique or hydrothermal synthesis) which has not been reported for Pb-V-I based apatites so far.

CONCLUSION

The development of a viable apatite based waste form for the immobilization of I-129 would be a significant contribution to the nuclear waste management community. In comparison to current proposed technology, apatite waste forms possess a significant advantage by providing substantial financial savings along the nuclear waste processing stream. By replacing current waste form technologies utilizing precious metals, such as Ag-exchanged zeolite, with lower cost metals, such as lead and calcium, the cost-efficiency of immobilizing iodine waste becomes much improved and much more viable. In the U.K., for instance, radioactive I-129 is currently being discharged into the sea. Considering possible future changes to regulatory practices, it is necessary to review strategies for developing durable waste forms for the immobilization of I-129 and apatites are a very viable candidate.

The development of apatite based waste forms could also prove beneficial for the immobilization of other existing radioactive isotopes. Because of the ability of apatite to incorporate various halides within its crystal structure, the future potential for immobilizing mixed halide waste is very feasible. By streamlining and consolidating the steps involved with collecting reprocessing plant off-gas, the potential for financial savings would again be improved substantially. Chloride-containing apatites, for instance, have already been proposed as a potential waste form for radioactive chloride waste. Considering that I-129 holds one of the longest half-life durations among the various HLW, a success in the immobilization of iodine would translate well to the immobilization of other radioactive waste.

Lastly, the ability of apatites to be synthesized by various methods would prove to be beneficial in the immobilization of large quantities of radioactive waste. By utilizing techniques, such as wet chemical synthesis, large quantities of apatite could be produced to meet the demands of the nuclear waste management community.

As can be seen, the investigation into the immobilization of iodine waste utilizing apatite waste forms is an ongoing process within the research community. Significant advancement has been made towards developing novel methods to synthesize apatite based ceramic waste forms, with particular emphasis on Pb-V-I and Ca-P-I systems. There still exist potential candidate waste forms that have not been explored, while novel low temperature synthesis methods need to be developed in order to produce chemically durable waste forms using a simplified process. Progress, however, certainly has been made and will continue to advance in the ongoing future.

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