Stabilization of Radionuclides and Metals into Spinels Using THOR® Fluidized Bed Steam Reforming – 12039

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ABSTRACT

Studsvik, Inc.'s Thermal Organic Reduction (THOR) Process has been operating for over 12 years in the treatment of radioactive liquid and solid wastes from commercial Nuclear Power Plants in the United States. A second THOR plant is starting operations in early 2012 for the treatment of radioactive wastes from US nuclear power research at US DOE's Idaho National Laboratory. THOR has long been recognized for its unique ability to substantially reduce the volume of radioactive wastes - via the removal of water and destruction of organics, nitrates/nitrites, etc.- and produce a dry, stable solid product while retaining extremely high amounts (>99.99%) of the incoming wastes' radioactivity [1]. Moreover, the THOR process has demonstrated the ability to produce radioactive waste forms with leach-resistance as good as or better than vitrified glass [2]. An additional facet of the technology which, to this point, has been marginalized is the production spinels that are essential for capturing volatile, leachable, and large radioactive and hazardous inorganic species. These spinels form from the wide variety of inorganics in the incoming waste feed and proprietary additives used in processing.

INTRODUCTION

Spinels are a class of minerals containing a face-centered cubic close-packed crystal structure with the standard structure of AE_2X_4. In a "normal-Spinel" A represents a divalent cation (e.g.-Fe^{2+}) occupying 1/8th of the available tetrahedral sites, E represents a trivalent cation (e.g.-Fe^{3+}) occupying half of the octahedral sites, and X is generally Oxygen - but can also be Sulfur or Selenium. However, there exists substantial variation in the composition and structure of minerals that are classified as spinels. This variability allows for the incorporation of many metals into the leach-resistant matrix without alteration to the THOR process. The THOR product has shown excellent durability in laboratory and regulatory testing. This apparently inherent durability is supported by the study of natural analogues wherein spinels are often found after weathering has removed the host rock. The durability of the spinel form is also evidenced by their use as refractory material, as an inert nuclear fuel matrix [3], in dielectric windows in fusion reactors [4], and in ceramic nuclear waste forms such as Synroc-D [5][6][7]. Spinel production within the THOR process has been verified by X-Ray diffraction [8]. Studies have shown that the REDOX condition maintained within THOR process primes metals for inclusion into spinel minerals [9]. Testing has shown that the waste form generated by the THOR process incorporates radioactive and hazardous metals into leach-resistance spinel structures, such as $FeCr_2O_4$, $CoAl_2O_4$, and $NiFe_2O_4$ to name a few.. These results demonstrate the potential use of THOR for the treatment of RCRA and TSCA regulated hazardous waste and/or mixed radioactive and hazardous wastes.

METHODS

Prior to discussing the formation of spinels in the THOR FBSR process, it is advantageous to explore the various types of spinels and the factors affecting spinel formation. The following subsections first provide an overview of spinels and then the THOR FBSR process for those readers not particularly familiar with the fields.

General Spinel Structure ($A^{2+}E^{3+}{}_2X_4$)

Spinels are a class of mixed metal-oxide ionic compounds with a simple crystal structure ($A^{tet}E_2{}^{oct}X_4$) where A normally represents a divalent cation (e.g.-Fe^{2+}), E normally represents a trivalent cation (e.g.-Fe^{3+}), and X is generally Oxygen -but can also be Sulfur or Selenium.

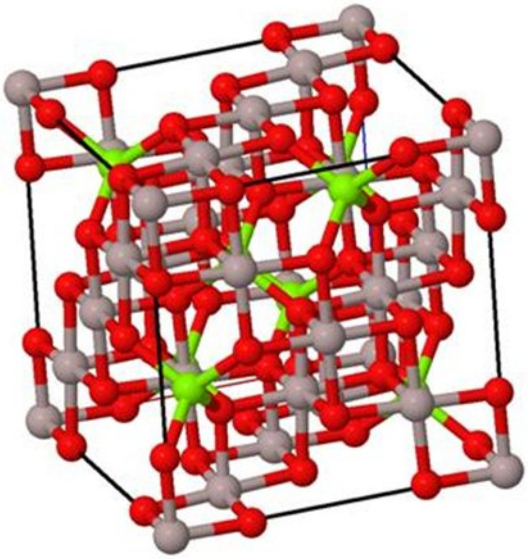

Fig 1. Basic Spinel Structure with Divalent Species in Green, Trivalent in Grey, and Oxygen/Sulfur in Red

In these so-called "normal 2-3 Spinels" divalent cations (A) occupy 1/8th of the tetrahedral sites and trivalent cations (E) occupy 1/2 of the octahedral sites. The structure consists of a nearly cubic closed-packed (fcc) array of 32 oxide ions, which forms 64 tetrahedral holes and 32 octahedral holes in one unit cell (containing eight formula units $(AE_2X_4)_8$).

Deviating from the basic Spinel are numerous structural modifications that lead to large variations in the properties of so-called "Spinels".

Spinel Electroneutrality

Electroneutrality limits the types of crystal structures that can be adopted by ionically bonded atoms by requiring that the crystal remain electrically neutral. Thus, specific cation-anion stoichiometries must be maintained in Spinels to preserve a net balance between positive and negative charges.

Spinel Cation Size

In general, the smaller cation will preferentially occupy the site of lower coordination (i.e. - tetrahedral site). However, other factors can negate this pattern as can be seen with the example of $MgAl_2O_4$ in which cation size is a secondary factor when the greater lattice energy of the smaller cation (Al^{3+}) is considered. In $MgAl_2O_4$ the smaller cation occupies the octahedral site in what is considered a normal Spinel structure. If cation size were the primary determinant, then $MgAl_2O_4$ would have an inverse Spinel structure.

Jahn-Teller Effect

The Jahn-Teller Theorem essentially states that any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy. The cooperative Jahn-Teller effect is known to cause phase transition among some Spinels from the cubic crystalline structure to a tetragonal Spinel. For octahedral coordination, susceptible species are d^4, d^9, and low spin d^7. For tetrahedral coordination, susceptible species are high spin d^2, d^5, d^7, and low spin d^4.

Crystal Field Stabilization Energies (CFSE)

The crystal field stabilization energy (CFSE) is the stability that results from placing a transition metal ion (such as hazardous metals and radionuclides) in the crystal field generated by a set of ligands. It arises due to the fact that when the d-orbitals are split in a ligand field some of them become lower in energy than before with respect to the barycenter in which all five d-orbitals are degenerate. CFSE is applicable when transition metals are incorporated into a Spinel structure. In general, the cation with higher CFSE energy in the octahedral site will occupy said site. The difference in CFSE in octahedral and tetrahedral sites is termed Octahedral Site Stabilization Energy (OSSE).

Normal 2-3 and 4-2 Spinels

Normal 2-3 Spinel structures usually take on a face centered cubic closed-packed structure. Divalent cations take up 1/8th of the tetrahedral “holes” while trivalent cations take up ½ of the octahedral “holes”. A typical 2-3 spinel is Trevorite ($NiFe_2O_4$), which can be useful for capturing the hazardous and potentially radioactive Ni (^{63}Ni) and radioactive ^{55}Fe.

In some Spinel systems the A site can incorporate a tetravalent cation (e.g.- Ti^{4+}) and the E site takes on divalent cations; such Spinels are called '4-2 Spinels'. Producing such spinels are useful for radioactive wastes that contain tetravalent cations, such as Cesium- and Strontium-capturing Titanium Nickel Ferrocyanides.

Inverse Spinels

Unlike the $A^{tet}E_2^{oct}X_4$ structure of normal spinels, inverse Spinels take on the $E^{tet}(AE)^{oct}X_4$ structure. Divalent cations occupy octahedral sites while half of the trivalent cations occupy tetrahedral voids. A typical inverse spinel is magnetite (Fe_3O_4) which may be more precisely written as $Fe^{+3}(Fe^{+2}Fe^{+3})O_4$.

Random Cation Arrangement

An important structural trait of Spinel compounds is the degree of cation disorder. Charge-compensating vacancies reside in the octahedral sites and increase with increasing cation disorder (randomness).In reality there exists a spectrum of cation distribution between the aforementioned 'normal 2-3 Spinel' and the 'inverse Spinel'. The arrangement of cations in Spinel structure can alternately be described as $(A_{(1-i)}E_i)_8(A_{(i/2)}E_{(1-(i/2))})_{16}X_{32}$, where i=0 would correspond to the 'normal 2-3 Spinel' and i=1 would correspond to the 'inverse Spinel'. A completely random distribution of divalent and trivalent cations occurs when i=2/3.

Degree of Ordering

Mineral waste forms contain varying degrees of crystallographic arrangement referred to as short-, medium-, and long-range order (SRO, MRO, LRO). Minerals produced by THOR FBSR (Spinels along with Alakli-Alumino-Silicates), Sintering, Hot and Cold Uniaxial Pressing, and Hot Isostatic Pressing all contain some degree of short-, medium-, and long-range order. Vitrified glasses contain SRO and MRO but no LRO.

Short-Range Order has a radius of influence ~1.6-3Å around a central atom or first nearest neighboring atoms. Medium-range order extends from roughly 3 to 6 Å (encompassing second and third-nearest neighbors around a central atom). Long-range order extends beyond the third-neighbor environments and gives the crystalline mineral structures their crystallographic periodicity [2].

Spinel Durability - Natural Analogs

The spinel form is widespread in geologic environments such as kimberlite and peridotite. Spinels are highly durable and often found after the host rock has been broken down via weathering [10]. Moreover, studies have shown that Spinels are durable in highly basic and acidic solutions [11] [12].

THOR FBSR Process

THOR fluidized bed steam reforming (FBSR) consists of a bed of proppant fluidized by an upward flow of superheated steam into which the liquid or slurried solid waste is injected. A reductant, typically some type of coal, is also added to the bed as a fuel source and to react with steam to create a reactive, reducing environment that produces N_2, H_2O, and CO_2 gases along with spinels and metal oxides.

As mentioned earlier, the nature of the fluidized bed allows for uniform physical and chemical conditions within the processing vessel. Thus, waste degradation and product formation reactions can be controlled so long as the reaction mechanics are understood. There exist four chemical environment characteristics that can affect waste degradation and product formation: 1) pressure; 2) temperature; 3) oxygen fugacity (REDOX condition); and 4) residence time.

Pressure

The pressure of FBSR is variable but is typically run slightly negative. This serves several purposes: 1) greatly reduces the risk for a leak of process gases out of the system; 2) provides a motive force for elutriating product from the FBSR; and 3) provides a motive force for process gases through the gas treatment system.
Thus, pressure is not varied as a means to control waste destruction and product formation. Rather, temperature and oxygen fugacity are varied at the pressure selected to obtain the desired results.

Temperature

The temperatures (650ºC to 850°C) utilized in FBSR treatment are comparatively mild considering the alternative waste treatment methods (e.g. - Vitrification, Hot Isostatic Pressing, Sintering). The mild temperatures prevent the release of even Cs and Tc, which have traditionally been considered to be highly volatile in thermal treatment processes. The temperature used for each application is part of a complex interplay between the processing variables. Temperature is controlled both spatially and temporally to properly control waste degradation and mineral production.

Some spinels will transition between an ordered and disordered state based on temperature. To illustrate, normal $MgAl_2O_4$ prevails at temperatures below 600 ºC but becomes more and more inverted concurrent with temperature rise [18][19]. On the other hand, Fe_3O_4 (magnetite) is "inverse" at low temperatures and progresses to virtually random distribution by 1450ºC [20]. In binary-spinels the cation distribution may be dependent on temperature [21], composition [22][23], or both [24][25][26]. Other spinels, (e.g. – chromites) show no temperature dependence [27].

Oxygen Fugacity

The oxygen fugacity maintained in the FBSR processes determines the REDOX state of the inorganic waste components. The oxygen fugacity in the THOR process is controlled by monitoring of gas composition exiting the FBSR and control of fluidizing gas composition and solid reductant addition. The FBSR is run in a chemically 'reducing' mode, however the sensitivity of the resultant REDOX state varies substantially by element. For example, the REDOX state of Manganese is readily reduced from Mn^{3+} to Mn^{2+} in the FBSR, but it is rather insensitive to further alterations in oxygen fugacity. Titanium is equally insensitive to oxygen fugacity modification but tends to remain in the Ti^{+4} state –as opposed to the reduced Ti^{+3}- under typical FBSR conditions. Chromium, on the other hand, is sensitive to variation in the oxygen fugacity of the FBSR, and is preferentially reduced to the Cr^{+3} form [9].

Residence Time

The height and diameter of a FBSR, the fluidizing gas velocity, bed material, waste injection method, and final mineral form selected all interplay to affect the residence time of waste within the reformer. As such, each FBSR system is designed to allow for proper residence time for waste destruction and mineral product formation for the given waste stream –including mixed phase wastes [28][29][30].

Waste Destruction Equations

As previously discussed, REDOX of the mineral products is a function of the overall oxygen fugacity of the THOR FBSR. Oxygen fugacity is primarily controlled through the use of reductants such as coal. These additives reduce the available oxygen while providing a fuel source for the process heat required for waste destruction and mineral product formation. In this section, the governing equations for waste destruction and Spinel formation are provided. For simplicity all equations will assume coal as the reductant.

For clarity, waste destruction in this instance refers to all aspects of a material that generates potential issues for disposal, namely: water, organics, and nitrates/nitrites. The temperatures of the THOR® process ensure that all water is removed from the waste and subsequent product. Decomposition of organics produces primarily elemental carbon, methane, carbon monoxide, and hydrogen gas.

$$CxHyOz \rightarrow C + CH4 + CO + H2, \text{etc.} \qquad \text{(Eq. 1)}$$

Steam, as fluidizing gas and from the waste feed, reacts with the carbon from decomposed organics and coal addition, via the water gas reaction to form a small amount of hydrogen gas and carbon monoxide.

$$H2O + C \rightarrow H2 + CO \qquad \text{(Eq. 2)}$$

Carbon monoxide is then oxidized to carbon dioxide via the concurrent reduction of steam to hydrogen gas, during the water gas shift reaction.

$$CO + H2O \leftrightarrow CO2 + H2 \qquad \text{(Eq. 3)}$$

Elemental carbon from coal and the decomposition of organic compounds is oxidized, forming carbon dioxide.

$$C + O2 \leftrightarrow CO2 \qquad \text{(Eq. 4)}$$

Carbon monoxide generated from organic decomposition and the water gas reaction is oxidized to carbon dioxide.

$$2CO + O2 \leftrightarrow 2CO2 \qquad \text{(Eq. 5)}$$

The small amount of hydrogen generated from organic decomposition, the water gas reaction, and the water gas shift reaction is oxidized to steam.

$$2H2 + O2 \leftrightarrow 2H2O \qquad \text{(Eq. 6)}$$

Equations 1, 2, and 3 are endothermic, so a small amount of oxygen is injected to achieve autothermal control of the process. The exothermic reactions of carbon, H_2, and CH_4 with oxygen generate more CO and CO_2. Heat from the exothermic oxidation reactions provides the process heat required to maintain bed temperature and drive the endothermic reactions. Complex hydrocarbons are not produced by THOR FBSR due to operations being maintained under an excess of steam.

In the fluidized bed steam reformer NO_X gases are produced from the thermal decomposition of nitrate compounds and are subsequently destroyed due to the presence of carbon, steam, and small amounts of carbon monoxide and hydrogen in the fluidized bed. Carbon from coal (and other organics) reacts with steam to form a small amount of carbon monoxide and hydrogen through the water gas and water gas shift reactions (Eq 2). Subsequently, the CO and H_2 produced from the water gas and water gas shift reactions together with carbon particles, reacts with NO_3 and NO_2 to produce water vapor and nitrogen (Eq 7-11):

$$2Ca(NO_3)_2 + 5C \rightarrow 2CaO + 2N_2 + 5CO_2 \qquad \text{(Eq. 7)}$$

$$4NaNO_3 + 5C \rightarrow 2Na_2O + 2N_2 + 5CO_2 \qquad \text{(Eq. 8)}$$

$$4NaNO_2 + 3C \rightarrow 2Na_2O + 2N_2 + 3CO_2 \qquad \text{(Eq. 9)}$$

$$2NO_3 + 2CO + 4H_2 \rightarrow N_2 + 4H_2O + 2CO_2 \qquad \text{(Eq. 10)}$$

$$2NO_2 + 2CO + 2H_2 \rightarrow N_2 + 2H_2O + 2CO_2 \qquad \text{(Eq. 11)}$$

Other nitrate compounds react directly with CO and/or H_2 and reduce to water vapor and nitrogen (Eq 12, 13):

$$NH_4NO_3 + H_2 \rightarrow N_2 + 3H_2O \qquad \text{(Eq. 12)}$$

$$2HNO_3 + 5H_2 \rightarrow N_2 + 6H_2O \qquad \text{(Eq. 13)}$$

Temperatures in the FBSR are low enough that no thermal NOx is produced; therefore, downstream NOx reduction equipment is not typically required.

Spinel Formation in the THOR FBSR Proces

As previously discussed, the primary components of Spinels are metals, Oxygen, and -if present- Selenium and Sulfur. The primary factor controlling spinel formation is the REDOX state of the metals. With the consistent exception of Ti, metals will generally not enter the spinel structure unless they are in the +2 or +3 state. As such, an overly oxidizing environment will preclude the formation of Spinels in favor of more leachable forms.

Cr will be used to demonstrate the Spinel formation in the THOR FBSR process. The elevated temperature and reducing atmosphere of the FBSR process will convert Cr^{+6} in a waste to Cr^{+3}. The reduced Chromium is then stabilized by incorporation into the spinel matrix as the (Co, Fe, Ni, Zn)Cr_2O_4 spinel. If the FBSR atmosphere is altered to be more oxidizing, then Chromate ($CrO^{2-}{}_4$) would be produced, resulting in decreased leach-resistance.

Stabilization of large concentrations of Cr, Fe, Ni, etc. into leach-resistant spinels by FBSR has been proven in engineering-scale demonstration programs for the US Department of Energy [2].

RESULTS

Leach testing has been performed by Jantzen et. al. to evaluate the ability of the FBSR process to capture and retain RCRA species in the final solid product. FBSR granular solids were collected from several Engineering Scale Technology Demonstrations (ESTD) and used in the Environmental Protection Agency (EPA) Toxic Characteristic Leaching Procedure (TCLP). The FBSR simulated input waste stream contained transition metals Chromium, Nickel, and Lead. The results indicated that the FBSR solids pass TCLP for Chromium, Nickel, and Lead release at the Universal Treatment Standard (UTS) limits. A portion of the Fe in the waste (can also be included as a process additive) forms the magnetite spinel host phase that sequesters Chromium as Cr^{3+} into its insoluble structure [31]. The magnetite spinel is also the host phase that sequesters Nickel as Ni^{2+}, where tetrahedral Fe^{2+} is replaced by Ni^{2+}. Lead directly forms the insoluble spinel Pb_3O_4.

An optical photograph of a typical granular solid from the FBSR process is shown in Figure 2 [32]. The small black particles dispersed throughout the solid product are magnetite particles.

Fig 2. Optical Photograph of FBSR Product. Black Particles are Magnetite

DISCUSSION

Spinels have been considered for a number of high radiation applications such as windows in fusion reactors, as a potential phase in inert fuel matrices, and as a nuclear waste form. The fact that the physical characteristics are not substantially degraded by irradiation makes spinels unique as a nuclear waste form [13]. In fact, radioactive and hazardous waste forms have leveraged the durability of the spinel structure to provide leach-resistance. However, care must be taken when applying these results to spinels produced in other processes. Spinel durability is dependent upon the specific spinels produced and any concurrent waste forms present. Incorporation of species in multiple phases can complicate determining the leach rate from radioactive waste forms, which would include spinels [7][14]. Thus, it can be expected that a pure spinel phase will have different leaching characteristics than those found in multiphase systems such as Synroc-D or the THOR FBSR process.

Synroc-D

Leach testing of Synroc-D with 23.8% Fe_2O_3 and 18.6% Al_2O_3 found no Fe and reduced Al content in the leachate which compared well with the other waste forms. It was proposed that ~70% of the Al was relegated to the Spinel phase thus accounting for its relative absence from the leachate. Thus, the durability of the spinel phase can exceed that of at least some radioactive waste forms [15].

Glass-Ceramics

Recycling of industrial wastes by incorporating the hazardous metals into glass-ceramics has been proposed as an alternative to disposal [16]. Testing of such glass-ceramics has shown the inherent durability of the spinel phase. However, care must be taken when applying these results to Spinels produced in other processes, as the glass-ceramics have been shown to have issues of contaminant migration to the glass-ceramic grain boundary [17].

Radioactive Metal Immobilization

In the field of radioactive waste Studsvik, Inc. has extensive experience producing leach-resistant waste forms from Ion Exchange Resins, Filters, and other commercially-generated radioactive waste for over 12 years. The flexibility of the technology has made it an attractive treatment option both domestically and internationally for a wide variety of applications. Spinels are an essential part of the leach-resistant waste forms demonstrated by Studsvik for such varied wastes as ion exchange resins from commercial nuclear power plants, INL's Sodium-Bearing Waste, Hanford's LAW, and WTP secondary waste, and SRS's Tank 48H waste.

Hazardous Waste Immobilization

An as-of-yet untapped utilization of spinels is in the hazardous waste field. The production of leach-resistant waste forms from hazardous Cr, Ni, etc. provides the potential of de-listing such hazardous wastes. The added benefit of the THOR process is the volume reduction and destruction of organics –including hazardous organic compounds.

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