TITLE: NUCLEAR WASTE PROCESSING BASED ON FOOF AND KrF_2

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ABSTRACT

A class of oxygen fluoride compounds and krypton difluoride show great promise in recovering and purifying plutonium and other actinides from nuclear waste and residues. Since 1983, a significant effort has been expended in three main areas of research; One area is the characterization of the reactive species and the fluorination reaction chemistry with various actinides. The second area is to develop efficient production methods for the active chemicals. The third area is actually in demonstrating application of these fluorinating agents to actinides recovery and purification. We have made substantial progress in all three areas and some of the highlights in our research effort will be discussed.

INTRODUCTION

Early in 1983, it was discovered that O$_2$F$_2$and O$_2$F can volatilize plutonium compounds as plutonium hexafluoride at ambient temperature [1,2]. Not long after this discovery it was demonstrated that KrF$_2$ had the same high reactivity towards plutonium as the two oxygen fluorides. Until then, fluoride atoms and also high temperature elemental fluorine were the only chemical species known to demonstrate this reactivity.

Our research on these potent fluorinating agents has several components. We characterize the chemical species responsible for the fluorination reaction, develop efficient production methods for the active chemicals, study the reaction mechanisms and kinetics with various actinide substrates, and apply these fluorinating agents to plutonium recovery and purification.

We recognized early on the potential benefits of the fluoride volatility process as a way of recovering and purifying actinides from various forms of nuclear waste and residues. Unlike some conventional aqueous and pyrochemical methods, the new method is viewed as a truly waste minimizing process with fewer process steps and lends to implementing remote and automated control, thus reducing worker radiation exposure. The advantage of recovering valuable energy resources without generating additional wastes justifies initial investment in research and modernization of nuclear processing facilities.

Main accomplishments are in the following areas; (1) complete characterization of the reactive species and some of their relevant fluorination chemistry with actinides, (2) development of efficient production methods of O$_2$F$_2$, and

(3) experimental verifications of actinide recovery and purification. In the present paper we will discuss some of the highlights in these areas and present our future directions in our research effort.

THE CHEMISTRY OF O_2F_2 AND KrF_2

The chemistry of oxygen fluorides has been studied since early 1960's, and a bulk of information on several well known compounds is summarized in references 3 and 4. However, it is only recently that we were able to fully characterize the formation and reaction kinetics of O_2F_2 and $O_2F[5]$. A dynamic equilibrium condition exists between O_2F_2 and O_2F represented by $O_2F + O_2F = O_2 F_2 + O_2$, and this equilibrium reaction shows that O_2 serves as the fluorine atom carrier and also determines the composition of the two species. The molecular structures of O_2F_2 and O_2F have been extensively studied by microwave and infrared spectroscopy by us and other researchers[6,7].

The O_2F and O_2F_2 equilibrium reaction shown above is a representation for gas phase compositions. Upon condensation of the reaction mixtures, however, O_2F_2 is the dominant species, regardless of the concentration of oxygen. Both species are thermally unstable. Their thermal stabilities were measured by recording half-life (the time required for the half of the original concentration to react in a reaction vessel in the absence of any reactants) as a function of temperature. Figure 1 shows an example of such measurements of O_2F_2 in the temperature range of 180 K and 295 K.

In a series of experiments conducted in our laboratory, known amounts of O_2F_2 were introduced into a reaction vessel and the concentrations of both O_2F_2 and O_2F were monitored as functions of temperature, time, oxygen content, and total pressure. Analyses of the data provided information on the equilibrium constants, dissociation kinetics, and bond energies[8,9]. The extreme thermal instability of these two spieces is clearly associated with their powerful fluorination reactivity.
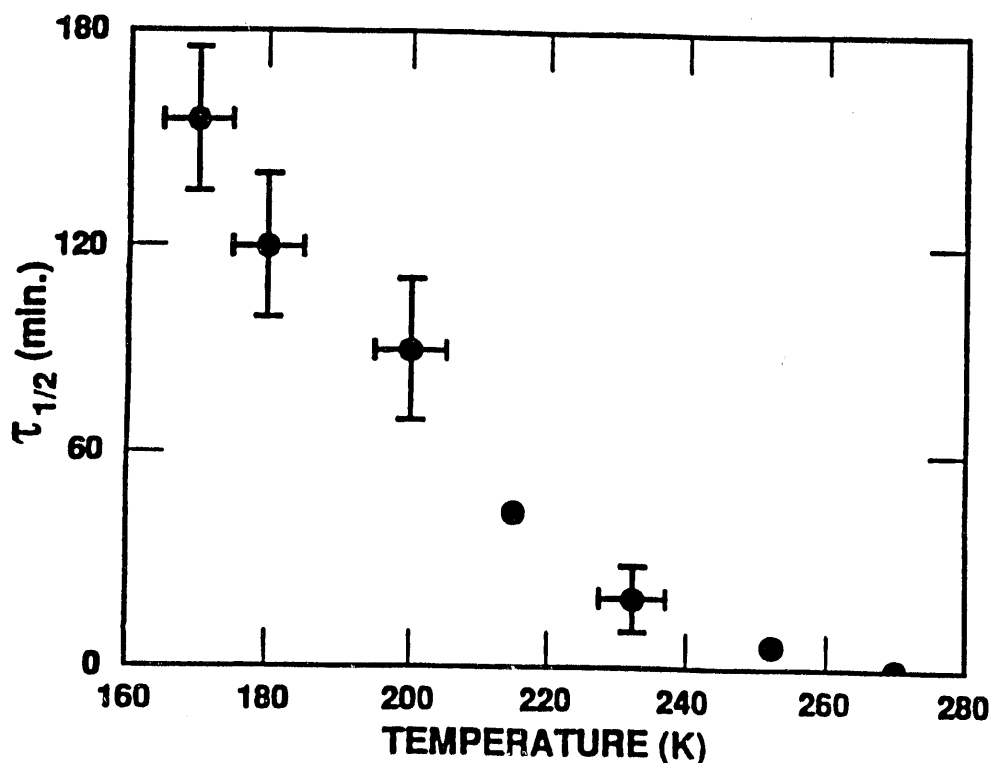

Figure 1: FOOF half-life as a function of temperature.

The formation of O_2F and subsequent O_2F_2 is enhanced at high pressures contrary to F atoms. This aspect and the ready transportability of oxygen fluorides make attractive their application to actinide fluorination. The fluorination reactivity of O_2F_2 is greater than O_2F on a molecule basis because each molecule of O_2F_2 produces two fluorine atoms as compared to one of O_2F. In both cases oxygen serves as F atom carrier.

KrF_2 displays the same high fluorination reactivity as O_2F_2 and O_2F. KrF_2 is relatively more stable than O_2F_2 as measured by their half-life times at room temperature, and, for this reason, more easily handled in storage and in reaction vessels. The formation of KrF_2, however, is facilitated only in condensed phases at cryogenic temperatures. This difficulty of producing multigram quantities of KrF_2 prevented us from conducting experiments on the scale that we were able to carry out with O_2F_2.

Unlike O_2F_2/O_2F, KrF_2 does not have the bound KrF counterpart, which makes its synthesis more difficult. Once formed, KrF_2 homogeneous half-lives are measured in days as compared to less than a second for O_2F_2 at ambient temperature. The fluorination reactivity of KrF_2 with actinide bearing substrates has been shown to be as high as that of O_2F_2. In addition, KrF_2 has the added advantage of better transportability to the reactive sites and its fluorination reaction can be precisely controlled at moderate temperatures below 100°C. Once the production difficulty is resolved, KrF_2 is expected to play an important role in nuclear waste processing.

Table 1 summarizes some of the properties of these powerful fluorinating agents. A comparison is made among F-atom, O_2F_2, O_2F, and KrF_2 in terms of their fluorination application.

Table 1: A Comparison of Plutonium Fluorinating Compounds

	F-Atom	O_2F_2	O_2F	KrF_2
Vapor Pressure	--	100 torr at 181 K[3]	--	127 torr at 298 K[11]
Bond Dissociation Energy (Kcal) [8,9]	--	18	18	18
Half-Life *	several seconds at 30 Torr total pressure	<1 sec at 295K at 295K	several seconds at 295K	several hours
Reactivity with actinides	fast	surface catalized decomposition - rate determining		
Transportability	poor	cooled transport line	poor	good
Preferred Synthetic Method	microwave	thermal	uv	hot-wire

* The time required for one half of the starting concentration to ract. This is not a well defined quantity which depends on many factors such as surface conditions, presence of other reactants, and total pressure.

SYNTHESIS OF O_2F_2 AND KrF_2

Commonly, these powerful fluorinating reagents were produced in small quantities by ultraviolet photodissociation or by electric or microwave discharge through the mixtures containing the reactants. Recently, a new scheme based on thermal dissociation of F_2 in the presence of O_2 or Kr was introduced as a promising alternative for producing large quantities of these reagents [10]. Because the products are unstable at reaction temperatures they have to be cooled instantly on cold surfaces and recovered as condensates at liquid nitrogen temperatures.

Elemental fluorine is thermally dissociated at temperatures above 600°C and the F atoms migrate to the adjacent cold surface where they combine with O_2 or Kr to form the respective compounds. We have expended a significant effort optimizing conditions for producing O_2F_2 by this method. Using a small scale device we have achieved a production rate of about 100 grams O_2F_2 per hour. The production rate for KrF_2 is about two orders of magnitude below that of O_2F_2.

APPLICATION TO ACTINIDE RECOVERY

Nuclear wastes are generated in a variety of forms. Our effort at Los Alamos for the past three years has concentrated on developing efficient processes for removing actinides, particularly plutonium, from several most common and abundant forms of nuclear residues and waste materials. It is also important that these materials are processed with overall waste reduction as the primary objective. Using oxides, various metal alloys, and halides of plutonium compounds, we have demonstrated that these forms will react with O_2F_2 room temperature to produce volatile at or below plutonium hexafluoride. The fluorination chemistry is represented by the following reaction:

$$Pu\ compounds + O_2F_2 \longrightarrow PuF_6 + O2 + solids.$$
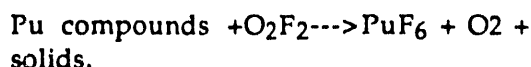
The reaction has been shown to be equally applicable to other heavy actinides. The resulting PuF_6 can be readily separated from the gaseous product stream by cryogenic distillation.

For the past one year our research effort has concentrated on exhaustive fluorination of several selected plutonium residues. The sample sizes were in the range of tens of gram quantities of bulk materials. We have successfully shown that a majority of the plutonium content was extracted with overall O_2F_2 utilization of a few percent, leaving behind solid residues which may be discarded for proper storage or burial. The recovered plutonium in the form of plutonium hexafluoride has chemical purity which eliminates further purification steps by conventional methods.

One specific waste form that we have studied extensively is incinerator ashes from nuclear processing plants. A typical ash sample contains a large number of elements as shown in Table 2. In a series of experiments we subjected a sample of this material to O_2F_2 fluorination and the results are shown in Figure 2. Successive batch addition of O_2F_2 produced plutonium hexafluoride, decreasing the plutonium content down to about 40 percent of the original value at the conclusion of experiment. The overall fluorination efficiency was low but for this fiducial experiment the reaction conditions were not necessarily optimized.

The fluorination reactions using gaseous oxidizing agents such as O_2F_2 and KrF_2 can be carried out most conveniently in a fluidized bed type of reactors. Samples to be processed can be loaded and removed by a screw feeder. The reagent diluted in an inert carrier gas is introduced through the filter at the bottom of the

Tabel 2: Typical Composition of Incinerator Ash*

Plutonium	0.138 g/g	Silicon	20.0%
Carbon	8.0%	Barium	2.0%
Hydrogen	0.6%	Sodium	3.0%
Nitrogen	370	Beryllium	1500
Chlorine	2.5%	Chromium	3.0%
Calcium	15.0%	Potassium	3.0%
Iron	15.0%	Copper	1.5%
Magnesium	10.0%	Nickle	3.0%
Phosphorus	<3000	Zinc	4.0%
Titanium	5.0%	Silver	500
Zirconium	5000	Vanadium	<100
Aluminum	5.0%	Cerium	<500
Cadmium	1000	Germanium	<100
Gallium	2000	Molybdenum	5000
Manganese	3.0%	Tungsten	<3000
Lead	2.0%	Cobalt	<100
Boron	1000	Hafnium	<300
Bismuth	<100	Tin	<300
Lithium	500	Niobium	<300
Yttrium	500	Strontium	<2000

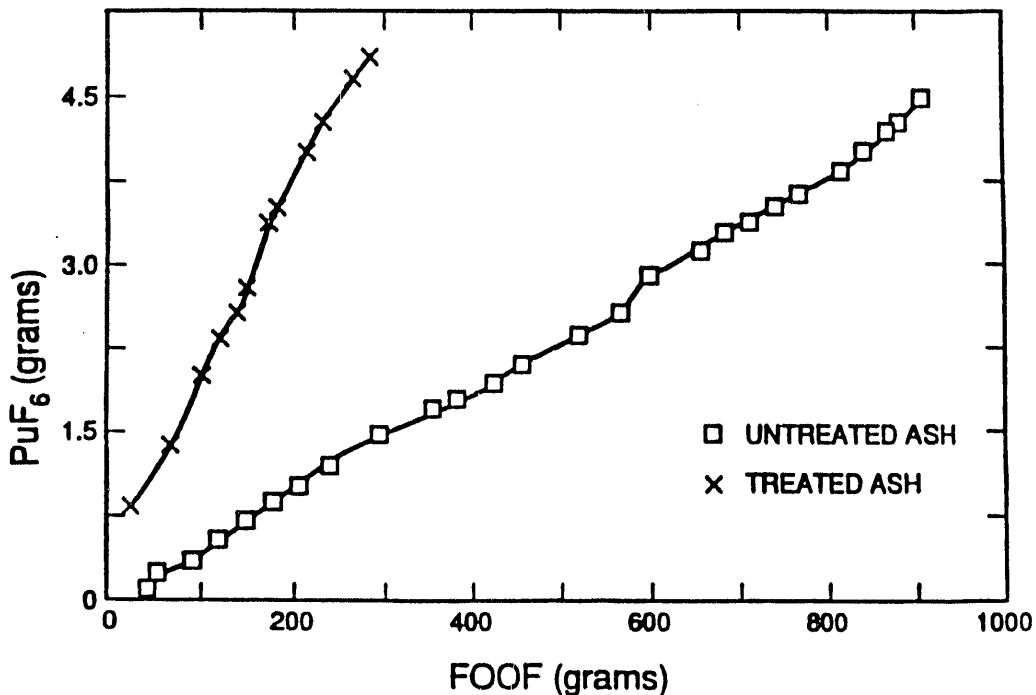* Total impurities are in excess of 120%

Figure 2: Fluorination of incinerator ash using FOOF.

reactor. The gaseous products are extracted continually at the top for further separation and purification. The process can be easily automated with remote control.

FUTURE DIRECTIONS

One area of our future activities is directed to improving the fluorination efficiencies by catalytic enhancement, pretreatment of the starting materials, and optimization of fluorination

efficiencies by optimization of fluorination reactor design. Another area which requires further developmental work is in better synthetic methods for KrF_2 and demonstration of process feasibility. Another important application is to decontamination of equipments, processing pipes, and containers, etc.

ACKNOWLEDGEMENTS

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