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PROCESSING OF GRAPHITE FUELS FOR URANIUM RECOVERY BY OXIDATION AND FLUORINATION

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ABSTRACT

A graphite fuel processing method utilizing oxygen or air oxidation and subsequent ash fluorination is proposed. Graphite oxidizer design, oxidizer control problems, and graphite-oxygen kinetics are discussed. Fluorination of the oxidizer ash and separation techniques for recovering uranium as UF_6 from other volatile fluorides resulting from the ash fluorination are also discussed. Evaluation of the proposed process and necessary additional experimental information are presented.

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1.0 INTRODUCTION

The use of graphite containing uranium as a fuel material in proposed high-temperature, gas-cooled nuclear reactors will present unique problems in fuel reprocessing. Several reprocessing schemes have been presented.[1]

This is a presentation of a processing scheme which uses oxidation of the graphite and fluorination of the resulting oxidation residue to recover the uranium. The proposed system is: (1) oxidation of the graphite to CO_2 with oxygen or air leaving a residue of uranium and other metal oxides; (2) fluorination of the residue to produce the fluorides of uranium and other metals, and (3) separation of UF_6 by a distillation or sorption technique.

2.0 OXIDATION OF GRAPHITE

Oxidation of graphite or carbon has been used as a routine industrial process for a considerable length of time. Combustion of graphite for recovery of included uranium has been successfully used in AEC installations for several years.[6,7] The oxidation of graphite has been studied extensively [2,3,4] and some excellent work has been done on the fundamental kinetics of the graphite-oxygen system.[5]

2.1 Reaction in the Graphite-Oxygen System

The kinetics of the reaction of oxygen with graphite can probably be described by considering four major contributing reactions:

$$C + 1/2O_2 \rightarrow CO \qquad (1)$$

$$C + O_2 \rightarrow CO_2 \qquad (2)$$

$$CO + 1/2O_2 \rightarrow CO_2 \qquad (3)$$

$$CO_2 + C \rightarrow 2CO \qquad (4)$$

The initial reactions of the oxygen-graphite system are probably equations (1) and (2). It has been found that both CO and CO_2 are products of the graphite-oxygen reaction and the CO/CO_2 product ratio is temperature dependent,[5]

$$CO/CO_2 = 10^{3.4} \exp(-12{,}400/RT) \ . \qquad (5)$$

Hence, CO_2 is the predominate species at low temperatures (< 500°C) predominates at higher temperatures when the initial reactions only are considered.

Although the initial reactions indicate that CO is an important product species at temperatures greater than 500°C, the reaction of CO with O_2 to form CO_2 (reaction 3) becomes important if excess O_2

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is used. The major product is CO_2 at temperature < 1200°C. The $CO-O_2$ reaction is predominately a "heterogeneous" reaction which occurs on the graphite surface at temperatures less than ~ 1000°C, and predominately a homogeneous gas phase reaction at higher temperatures. (This results in the blue glow sometimes seen above beds of graphite or carbon which are being burned.) It is probable that if excess oxygen is used in graphite burning, the predominate product will be CO_2 in the temperature range of interest for such a process, 800-1200°C.

At temperatures greater than ~ 1200°C, the $C-CO_2$ reaction (reaction 4) becomes important when deep beds of graphite are used. This reaction will not only accelerate the carbon oxidation rate but will also compete with the CO oxidation to tend towards more CO in the product gas.

Thus, a rather complex reaction system arises in which a combination of temperature, oxygen excess, and graphite bed depth, influences the amount and type of reaction product. If CO_2 is the desired reaction product, control of the process is relatively simple since excess oxygen tends to be the controlling parameter. This type of control is carried out routinely in industrial processes, such as coal burning and at AEC sites in which graphite burning is carried out.[6,7]

Recent work by Scott[8] shows that deep beds of graphite-uranium fuels can be oxidized with oxygen in the temperature range of 1000-1200°C and the effluent CO concentration can be controlled by the amount of oxygen excess.

2.2 Reaction Kinetics of the Graphite-Oxygen System

In general, heterogeneous reaction rates involving porous solids and fluids may be controlled by one or more of three major mechanisms:

1. Mass transport of the reacting gas from the bulk gas to the reaction site and mass transport of the reaction products from the reaction site to the bulk gas.

2. Sorption or desorption of reactants or products from active sites.

3. Reaction of the sorbed reactant at the reaction site.

In the graphite-oxygen reaction, reaction control appears to be mainly by mechanisms (2) and (3) at temperatures less than ~ 400°C and by mechanism (1) at temperatures greater than 900°C.[4] All three mechanisms could then contribute to reaction control in the intermediate temperature range.

A correlation of presently available kinetics data for the graphite-oxygen reaction has been made by Prados,[4]

$$k = 7.24 \times 10^9 \exp(-22{,}100/T) \qquad (6)$$

where,

k = rate constant for "chemical" step in graphite oxidation

T = absolute temperature, °K

This correlation indicates that if mass transfer is not a factor, and for normal types of graphite, the reaction rate of graphite in one atmosphere of oxygen at temperatures greater than 800°C will be sufficient to completely react the graphite in one hour. Recent experimental work has shown that two hours is sufficient to completely oxidize graphite from graphite-uranium fuels in the temperature range of 1000-1200°C.[8]

2.3 Hazards in the Graphite-oxygen Reaction

Two potential hazards exist in "graphite burning" operations which have historically been routinely handled by fairly simple control devices. The hazards are (1) possibility of explosive mixtures of $CO-O_2$ in the graphite burning system, and (2) possibility of graphite dust buildup which in an oxygen atmosphere could result in an explosion. The CO hazard can be controlled by monitoring the reactor effluent for CO and always using excess O_2 (lower explosive limit for CO in air is 12.5%). This procedure has been used in the Y-12 plant with success.[6] The "dusting" problem must be controlled by proper reactor design and by introducing the graphite charge as large particles (> 100 mesh). Los Alamos has successfully controlled this problem although they routinely introduce "graphite flour" as the feed material.[7]

3.0 FLUORINATION OF OXIDIZER ASH AND URANIUM RECOVERY

The ash from the graphite fuel oxidation step will contain uranium oxide (probably U_3O_8), oxides of metals present in the original fuel, fission product oxides, and possibly metal carbides.

3.1 Fluorination of Ash

Treatment of the ash from the oxidation step with elemental fluorine at 200-500°C will result in the formation of UF_6,

$$U_3O_8 + 17F_2 \rightarrow 3UF_6 + 8F_2O \ , \qquad (5)$$

other metal fluorides both volatile and nonvolatile, and oxygen fluoride (OF_2). Traces of carbon or carbides will also react to form fluorocarbons (primarily CF_4). No difficulty should be encountered in fluorinating ash for which the products of fluorination are predominately gases at fluorination conditions. Problems with slagging may be anticipated when the resulting metal fluoride is molten at the reactor operating conditions and difficulty in uranium removal might be encountered if a large fraction of the products of the fluorination are solids. A fused salt technique may then be necessary.

For many graphite fuels of interest the only metal fluorides which do not boil below 400°C will be fission product fluorides. Since the quantity of the fission product fluorides will be small, the only problem associated with them will be their buildup in the reactor system.

The fluorination of material somewhat comparable to the graphite oxidation ash, crude uranium ore concentrates, has been studied at ORGDP.[9] It is felt that technology developed at that site would be usable in the design of a fluorination system for this application.

It should be noted that if no metal carbides are present, HF might be used to volatilize some of the nonuranium metal oxides.

3.2 Uranium Purification

Two methods are available for the separation of UF_6 from other metal fluorides and oxyfluorides. These are (1) distillation, and (2) NaF sorption.

3.21 Separation by Distillation

Considerable work on the distillation of impure UF_6 has been reported.[10,11] Satisfactory separation has been demonstrated at several major installations. These include ORGDP,[11,12] Argonne National Laboratory, Allied Chemical Corp., and others. The separation of fluorides such as NbF_5, CrF_5, Ru-Fluorides, I-Fluorides, etc., from UF_6 can be made in a straightforward manner by distillation. Some difficulty has been encountered in distillation separation of molybdenum hexafluoride, vanadium pentafluoride, and vanadium oxyfluoride from UF_6; however, this technique is possible and has been demonstrated.

3.22 Separation by NaF Sorption

The removal of most contaminants of UF_6 can be easily effected by the use of NaF. Uranium hexafluoride complexes strongly with NaF at temperatures below 300°C so that separation of noncomplexing impurities is accomplished by passing the gases through a single NaF trap.

Many volatile fluorides form NaF complexes for which the dissociation pressure is highly temperature dependent. By proper temperature control in the presence of an inert gas purge the volatile fluorides can be differentially separated from each other, or from a single material such as UF_6. Reuse of the NaF for a number of cycles is possible.

Sodium fluoride sorption is particularly applicable to fuels of low burnup if the material of construction does not contribute volatile fluorides which have properties similar to uranium fluorides.

4.0 OXIDIZER-FLUORINATOR DESIGN

Two process design schemes can be used for this system: (1) a single vessel for both the oxidation and fluorination steps, and (2) separate vessels for the oxidation and fluorination steps with means of solid transport between the two vessels.

4.1 Design Criteria

The fuel oxidizing system must be capable of containing the graphite-oxygen environment, controlling the temperature by means of removing the heat of reaction of the graphite burning, and maintaining an oxygen excess in the oxidizer effluent to prevent buildup of carbon monoxide.

The ash fluorination system must be capable of containing the ash-fluorine environment and control the temperature by heat introduction or removal.

There must be provision in the system for processing the off-gas from the oxidation and fluorination steps to prevent escape of uranium and fission products and to separate the uranium from the fission products and other contaminants.

4.2 Separate Oxidizer Vessel

If separate oxidizing and fluorinating vessels are used, the process control problems are reduced; however, there must be a means of transfer of the resulting solid ash from the oxidizer to the fluorinator.

Design of the oxidizer would be relatively simple. The oxidizing vessel would be composed of a metallic shell (ferrous metal) which contained a grate, to hold the bed of graphite fuel, external cooling, probably by a water jacket, and an ignition system composed of a Calrod, resistance heated "fuse," or external heating (Fig. 1). The oxidizing gas would be metered by a rotameter or orifice meter which would be coupled to an O_2 or CO monitoring device in the off-gas. The bottom of the vessel would receive the resulting ash and a porous metal filter would be used to prevent fine solids from carryover to the final off-gas treatment system. There would have to be provisions for removing the solid product from the vessel for transfer to the fluorinator.

4.3 Separate Fluorinating Vessel

A separate fluorinating vessel would have provisions for containing a bed of ash for fluorination (Fig. 1) by either pure elemental fluorine or diluted fluorine. There would have to be provisions for initially heating the vessel to reaction temperature (probably 400-600°C) and maintaining that temperature during fluorination by gas dilution or by heat addition or removal. The material of construction for such a vessel would probably be nickel. There would be a necessity for gas-phase filtration to prevent solids removal from the reactor. Reactor control would be achieved by fluorine flow control and external reactor heating or cooling.

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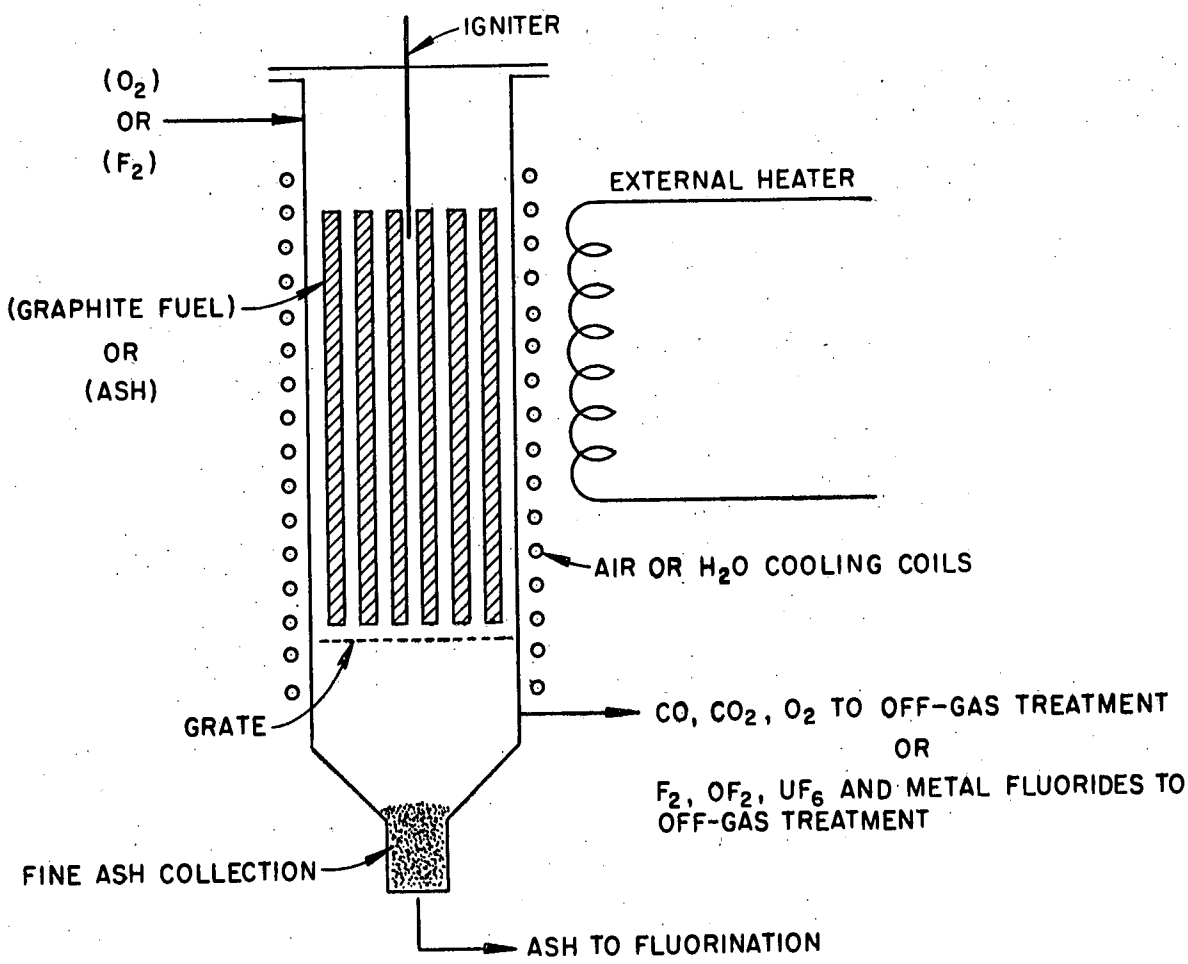

Fig. 1. Reaction Vessel.

4.4 Combination Oxidation and Fluorination Vessel

A vessel designed for both process steps would have to contain provisions necessary for each individual step. The vessel would probably be nickel, with both an external heating and cooling source and the necessary gas metering and off-gas monitoring devices to safely control both process steps (Fig. 1). In recent experimental work, it was found that the ash from the oxidation step tended to remain in the oxidation vessel above the grate.[8] Since the ash remained in place it would probably be possible to use the same vessel for fluorination.

4.5 Reactor Off-gas Treatment

The off-gas treatment for the oxidation step could be composed of process steps for scrubbing and filtering the off-gas (predominately CO_2 and O_2) to remove radioactivity prior to releasing it to the atmosphere. If radioactivity was sufficiently low, only filtration would be sufficient.

The off-gas treatment for the fluorination step would provide for removal of volatile uranium and impurity metal fluorides by cold-trapping or sorption prior to scrubbing or fixed bed reaction to remove excess fluorine. The uranium fluorides, fission product fluorides and other fluorides removed by cold-trapping or sorption would then have to be further processed by distillation or sorption to purify the uranium fluoride.

4.6 Additional Experimental Information Necessary for Adequate Design

There are several portions of the process design for such a process which would require additional experimental data. These include:

1. Process control and effect of process variables for the fixed bed oxidizer.

2. Kinetics of the fluorination of the anticipated components of the oxidizer ash.

3. Process control of the fluorination process.

4. Evaluation of the distillation and sorption purification steps for materials of interest.

5. Treatment of the off-gas from the process prior to release to the atmosphere.

5.0 PROCESS EVALUATION

There is sufficient information available to indicate that the oxidation-fluorination processing method for recovery of uranium from graphite-uranium fuels appears promising. Proper economic evaluation of the process cannot be made until additional development work has been done. It will be necessary to study the basic chemistry of the process, to investigate process control methods, to study heat removal and temperature control, and to obtain performance information on prototype equipment.

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