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THE CHEMICAL PROCESSING OF TWO-REGION AQUEOUS HOMOGENEOUS REACTORS

by

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Presented at
The First Winter Meeting-American Nuclear Society
Washington, D. C. - December 10-12, 1956

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THE CHEMICAL PROCESSING OF TWO-REGION AQUEOUS HOMOGENEOUS REACTORS

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A promising scheme for the chemical processing of a thorium breeder reactor of the two-region aqueous homogeneous type consists of the following operations: concentration of insoluble fission and corrosion products from the core system into a small volume of fuel solution, combining this slurry with irradiated thorium oxide slurry taken from the blanket, recovery of D_2O by evaporation, dissolution of the thorium and uranium in HNO_3 , and after a suitable cooling period recovery of the uranium and thorium by solvent extraction for return to the reactor. The use of a hydroclone and underflow container arrangement for concentrating insoluble fission and corrosion products under simulated reactor conditions has been successfully demonstrated on dynamic loops. Solids concentration factors of greater than 10^3 were demonstrated, and equilibrium solids concentration in the circulating solution of less than 1 ppm were attained in these tests. A problem yet to be resolved is the tendency of the solids to deposit in the reactor system. However, present data indicate that proper design and operation will minimize solids deposition in the reactor and that the insoluble impurities can be effectively removed by the hydroclone.

An alternate method of processing the slurry removed from the core system by the hydroclone consists of removing the room temperature insolubles by centrifugation, recovering the uranium from the supernatant by peroxide precipitation, thermal decomposition of the uranyl peroxide in dilute deuterated sulfuric acid to produce reactor fuel. This method has been successfully tested on a laboratory scale using a simulated hydroclone underflow slurry. The results of laboratory and loop studies of iodine chemistry indicated that iodine is sufficiently volatile under reactor conditions to be removed by gas stripping. The effect of radiation, temperature and other fission products on iodine valence have been studied.

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THE CHEMICAL PROCESSING OF TWO-REGION AQUEOUS HOMOGENEOUS REACTORS

by

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Based on work by members of the Chemical Technology and Reactor Experimental Engineering Divisions of Oak Ridge National Laboratory and Vitro Laboratories.

A two-region thorium breeder reactor of the aqueous homogeneous type is being developed at Oak Ridge National Laboratory as a promising source of economic power.¹ Such reactors have a central core containing the fuel surrounded by a blanket of thorium. The fuel is a heavy water solution of $U^{233}O_2SO_4$, and the blanket may be composed of ThO_2 suspended in heavy water. This configuration permits design of a small, high specific power reactor with good neutron economy. Such a reactor, 10 ft in diameter, can be operated at 450 MW and produce 21% net more U-233 in the blanket than is consumed in the core, provided the fuel solution is kept free of neutron poisons. A neutron poison level of 6% appears consistent with present chemical processing technology, and the reactor can be expected to produce about 15% excess U-233.

One outstanding advantage of aqueous homogeneous reactors is the inherent simplicity of chemical processing and fuel reconstitution. This is of particular importance for breeder reactors, since they depend so heavily on processing for removal of neutron poisons. In the case of this thorium breeder reactor various methods of processing have been evaluated in laboratory scouting work and an attractive scheme, which combines removal of insoluble impurities from the fuel by hydroclones with solvent extraction for simultaneous blanket processing and recovery of uranium from the hydroclone underflow has been outlined.^{2,3} This scheme of processing is illustrated in Fig. 1. Approximately one reactor volume, 10,000 liters, of fuel solution per day is passed through a hydroclone separator. The insoluble fission and corrosion products are concentrated

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Fig. 1. SCHEMATIC FLOWSHEET FOR THORIUM BREEDER REACTOR PROCESSING

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into 100 liters of fuel solution by the hydroclone. This 100 liters of slurry is then combined with ThO_2 slurry, 110 kilograms of thorium per day, withdrawn from the reactor blanket. Following the recovery of D_2O from these materials by evaporation and drying the material can be dissolved in HNO_3 , and the thorium and U-233 isolated for return to the reactor by solvent extraction. Such a scheme is economically feasible. The technical feasibility of the solvent extraction portion of this scheme and the design and operating characteristics of hydroclone separators have been discussed in previous papers.^{4,5} This paper, which is in the form of a progress report, discusses the anticipated problems in removing insoluble fission and corrosion products from the reactor fuel system with hydroclones, an alternate scheme to solvent extraction for processing the hydroclone underflow, and recent results of iodine chemistry studies under simulated reactor conditions.

REMOVAL OF INSOLUBLES FROM REACTOR CORE SYSTEM

There appears to be a tendency for insoluble materials suspended in reactor fuel solution to plate out or deposit on the surfaces within aqueous high pressure, high temperature systems. This has been consistently observed in autoclave and dynamic loop tests on the 1 liter to 100 liter scale. As observed in these tests, there are three distinct methods of deposition:

1. Crystallization of sulfate salts, such as the rare earth sulfates, on surfaces which are hotter than the fuel solution.
2. Adsorption of solids particles on the walls independent of relative temperature.
3. Gravity settling of solids in regions of low turbulence.

Undoubtedly, there is also true chemical sorption on the oxide films within the systems, but this does not appear significant in comparison with the amount of material deposited by the above mechanisms.

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In autoclave tests, the rare earth sulfate precipitates did not deposit on surfaces at the same temperature or slightly cooler than the solution. Well formed crystals of rare earth sulfates grew on metal surfaces hotter than the solution containing the rare earths. In these same tests iron and chromium oxides were observed to collect on the surfaces with an even distribution independent of relative temperature.

In small loops, about 5 liters in size, equipped with a hydroclone and underflow pot and which contained no large stagnant regions, about 15% of precipitated rare earth sulfates were recovered in the hydroclone underflow and essentially all the remaining insoluble rare earths were deposited on externally heated surfaces within the loop. In these tests the equilibrium amount of rare earths in solution in the loop corresponded roughly to the solubility at the temperature of the heated wall. In these same tests, 50 to 85% of ZrO_2 , a typical insoluble corrosion product oxide, formed by hydrolysis of $Zr(SO_4)_2$ inside the loop was recovered in the hydroclone underflow with the remaining ZrO_2 rather evenly distributed about the loop.

Further tests were carried out in two larger loops. One, the HRT mock-up, was constructed of full scale Homogeneous Reactor Test (5 MW prototype of a two-region homogeneous reactor) components except for a much smaller heat exchanger and no reactor vessel (see Fig. 2). This loop had a capacity of 80 liters, the solution was circulated at 400 gpm, and the flow through the hydroclone was 2 liters per minute. The other loop had the same circulation rate and contained 30 liters of solution, but was a simple loop of pipe with no horizontal stagnant regions (see Fig. 3). The hydroclone circuit for this loop was the actual HRT Chemical Plant (see next section). The flow through the hydroclone in this case was 3 liters per minute. The tests were conducted by injecting into these loops under simulated reactor conditions a mixture of Fe_2O_3 , Cr_2O_3 and ZrO_2 expected to be formed by corrosion in the core system of a thorium breeder reactor. The experiments were carried out with and without the hydroclone operating.

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Fig. 2. HRT MOCK-UP SCHEMATIC

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Fig. 3. TEST LOOP FOR HRT CHEMICAL PLANT.

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When the hydroclone was not operated, the simulated fission and corrosion products disappeared from the circulating stream of the HRT mock-up with a half-period of 2.5 hr (see Fig. 4). When the hydroclone was in operation, the half-period was 1.2 hr. From these results it was concluded that the half-period for solids removal by the hydroclone alone was 2.3 hr and that the hydroclone efficiency was about 20%. In the simpler loop, without the hydroclone operating the half-period for the disappearance of simulated fission and corrosion products was 11 hr, and with the chemical plant hydroclone operating, 1 hr. The chemical plant efficiency for solids removal as calculated from these results was 25%. This is in close agreement with the mock-up results.

In the above tests using a 0.4 in. hydroclone at 250 to 300°C with pressure drops of 15 psi or greater across the hydroclone, concentration factors* of from 70 to greater than 1000 were obtained for the simulated corrosion products. For the removal of solids from the core system of a two-region reactor a concentration factor of 30 is adequate. Based on these data, the performance of the hydroclone as a solids concentrator appears entirely satisfactory for this application.

The difference in solids behavior in the two loops is partially due to collection of solids in the non-turbulent horizontal pressurizer header of the mock-up. A large deposit of solids was found, apparently settled out by gravity, in this horizontal run of pipe after the runs were completed. No stagnant regions were present in the simple loop. However, this loop had a smaller surface area in contact with the solution than the mock-up and further experiments will be required to differentiate between adsorption of solids and gravity settling.

A concentrated solution of mixed rare earth sulfates traced with Nd^{147} was also injected into the HRT mock-up. Of the rare earths that precipitated in the loop, as determined by the tracer method, about 75% were removed by the hydroclone. The hydroclone concentration factor observed for the rare earth sulfates was greater than 100 in this test. In this case the heat exchanger represented a hot spot in the loop since

* Concentration factor as used here means the concentration of solids in the underflow receiver compared to the solids concentration in the hydroclone feed.

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Fig. 4. BEHAVIOR OF SOLIDS IN THE HRT MOCKUP

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the loop was heated by high pressure steam on the water side of the exchanger. The missing precipitated rare earths were not located, but from experience with the smaller systems they collected on the heated surface. In the reactor, the only surface expected to be hotter than the fuel solution is the core tank which will be exposed to intense gamma and neutron heating. However, in in-pile loops there is no tendency for insolubles to deposit on materials exposed to intense radiation, and for this reason no appreciable deposition of rare earths or corrosion products is expected in the high flux region of the reactor.

In none of the mock-up tests was any evidence found that the solids accumulated in the low pressure system. There were indications that lowering the system temperature to room temperature and then returning to operating conditions resuspended a large fraction of the material deposited in the high pressure system.

From these experiments, it was concluded that future aqueous homogeneous reactors must be designed to eliminate regions of low flow rate in horizontal runs of pipe which can trap solids by sedimentation. Even in properly designed reactors there will be a significant accumulation of solids in the system by solids adsorbing on the materials of construction, but this may be expected to reach an equilibrium where the solids will flake off as rapidly as they deposit. Further experiments are required to establish whether this accumulation of solids will be sufficient to interfere with heat transfer and fluid flow in the reactor system. These studies are planned for the dynamic loop and in the HRT Chemical Plant which is described in the next section.

HRT CHEMICAL PLANT

The HRT is a 5 MW prototype of a two-region homogeneous reactor.⁶ The core system will contain about 500 liters of fuel solution. The HRT Chemical Plant has been installed as a by-pass around the reactor heat exchanger (see Fig. 5). The major components of the chemical plant are a heater to compensate for heat losses, a screen to protect

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Fig. 5. SCHEMATIC OF HRT CHEMICAL PLANT

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the hydroclone from plugging, the hydroclone with a 2.5 gal underflow receiver, and a canned rotor pump to supply the pressure drop across the hydroclone. This system is designed to operate at 300°C under 2000 psi total pressure. The flow through the hydroclone will be 3 liters per minute, so that one reactor volume will pass through the hydroclone every 3 hr. Once a week the chemical plant will be valved off from the reactor, the contents cooled, and dropped to a tantalum lined vessel. From this vessel the D₂O will be recovered by evaporation and the residue sampled after dissolution in 10.8 M H₂SO₄. This will permit accurate determination of the fission and corrosion products removed from the reactor by the hydroclone.

The process equipment is contained in a concrete cell 21 ft deep, 12 ft wide and 24 ft long (see Fig. 6A). This cell is separated from the reactor by 5 ft of heavy concrete and from the operating areas by 4 ft of heavy concrete. The cell is lined with 3/4 in. steel plate, and is designed to withstand an internal pressure of 50 psig with essentially no leakage to the atmosphere. This is sufficient to contain the reactor contents in case of a rupture of the high pressure equipment. The top closure is made by a welded membrane in between the two sets of roof plugs that form the top shield.

The plant is designed so that the pump, heater, screen, and hydroclone can be easily replaced by underwater maintenance procedures. The hydroclone is contained in a flange mounted on the 2-1/2 gal underflow receiver. The heater and pump are also flanged into the system. The hydroclone is 0.4 in. internal diameter, 1.5 in. long and lined with titanium to resist abrasion (see Fig. 6). A similar hydroclone was operated on a 300°C loop for 4000 hr with no significant erosion taking place. The pump is a Westinghouse canned rotor pump design for 300°C, 2000 psi operation, and will deliver 1 gpm at 100 ft of head with a 60 cycle power supply. A variable frequency power supply for this pump is used to control the flow rate through the hydroclone circuit.

The equipment is connected in such a manner that when valved off

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Fig. 6A HRT Chemical Plant High Pressure Cell

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FIG. 6. CROSS SECTION OF INTEGRALLY FLANGED HYDROCLONE.

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from the reactor the pump can be used to circulate the underflow receiver contents over the screen to flush off any large particles and through the heater to dissolve any rare earth sulfates that may have accumulated on the heated surface. A sampler is provided to sample the underflow receiver contents and the hydroclone overflow. The core solution fed to the hydroclone is sampled in the reactor circuit.

The underflow receiver temperature is controlled by a circulating stream of heated air. The mechanical valves used in the plant are pneumatically operated, bellow sealed and are backed up with freeze plugs to eliminate leakage. The freeze plugs are made by coiling stainless steel tubing, through which a refrigerant can be passed around the pipe. In many lines freeze plugs alone are used. This is possible where the line can be frozen with no liquid flowing through it. It was not found possible to freeze lines through which more than 5 ml/min of solution was flowing.

The plant is designed to demonstrate the proposed core process only up through heavy water recovery. The dissolution of insolubles in H_2SO_4 is intended only as an analytical method. In actual processing of a reactor, the uranium and soluble fission products need only be leached from the insolubles with HNO_3 since laboratory tests indicate only 0.1% of the uranium in the underflow receiver contents was HNO_3 insoluble.

The program planned for this plant is aimed at establishing the feasibility of removing insolubles from the reactor fuel system with hydroclones and obtaining data on the chemistry of fission and corrosion products under actual reactor conditions.

URANIUM RECOVERY BY PEROXIDE PRECIPITATION

For an isolated reactor or small reactor station, a considerable savings could be effected by a simple, cheap clean-up of the uranium from the hydroclone underflow. In such a situation the irradiated ThO_2

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from the blanket would be packaged in shielded containers and shipped to a central solvent extraction plant for processing. Peroxide precipitation is one attractive method for recovering the uranium from the hydroclone underflow sufficiently decontaminated for return to the reactor.

This method consists of removing, by centrifugation and washing at room temperature, the insoluble fission and corrosion products such as the oxides of Zr, Fe, Cr and Nb; selective precipitation of uranium as UO_4 from the supernatant, thermal decomposition of the UO_4 in a dilute solution of D_2SO_4 to provide a suitable fuel solution for return to the reactor core (see Fig. 7).

The precipitation of UO_4 under simulated process conditions was tested on a laboratory scale (see Fig. 8). In these tests it was shown that 99.9% of the uranium could be recovered with a separation factor of greater than 10 from nickel, rare earths, and alkali metals. The UO_4 precipitate was easily converted to a UO_2SO_4 solution by thermal decomposition in the presence of stoichiometric H_2SO_4 in the form of dilute H_2SO_4 .

CHEMISTRY OF IODINE

Studies of the chemistry of iodine under simulated reactor conditions have been carried out in autoclaves and a dynamic loop.⁷ At 300°C with an oxygen atmosphere it was found that at equilibrium about 85% of the iodine in 0.02 M UO_2SO_4 solution was present as the elemental form, and that the distribution coefficient for elemental iodine between the vapor and liquid phase was 7 on a mole fraction basis. The remaining 15% of the iodine was in the iodate form. Experiments carried out under Co^{60} gamma irradiation at 250°C indicated that radiation tends to shift the equilibrium in favor of the elemental form. Addition of simulated reactor corrosion and fission products, other than ruthenium, had no detectable effect on the iodine valence distribution or volatility. At a concentration

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Fig. 7. UNDERFLOW PROCESSING BY UO_4 PRECIPITATION.

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Fig. 8. SOLUBILITY OF UO_4 vs pH

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five times that expected in the reactor, ruthenium fixed essentially all the iodine in the liquid phase. However, this was partially off-set by the presence of hydrogen gas and gamma radiation. From these data it was concluded that iodine will be sufficiently volatile to be removed from the reactor by gas stripping at elevated temperature. This was confirmed in the absence of radiation by dynamic loop tests in which iodine, injected into the system as either iodide or iodate, was effectively removed by gas (O_2 and water vapor) stripping at $250^\circ C$.

In an actual reactor this stripping may be accomplished in two ways. If sufficient copper sulfate catalyst is added to recombine all the radiolytic gas as it is formed, the iodine can be stripped in a high pressure system using oxygen as the stripping gas.³ If, however, some radiolytic gas is allowed to form in the reactor, this gas will serve to strip I, Xe and Kr from the reactor fuel solution.

One proposed method of removing I, Xe and Kr from such a radiolytic gas stream is to let the gas down to atmospheric pressure, separate out entrained fuel solution, and recombine the D_2 and O_2 catalytically. Xe and Kr would emerge as noncondensables along with excess O_2 when the water vapor from the recombiner is condensed at $65^\circ C$. However, experimental data indicate that iodine would be in the condensate since the vapor-liquid distribution coefficient for iodine under these conditions is only 0.01 on a mole fraction basis.

Some of the iodine will also follow the entrained fuel solution to the dump tank from the entrainment separator. Under the conditions of the entrainment separator and dump tank (these contain fuel solution at $100^\circ C$ and one atmosphere of pressure), elemental iodine has a mole fraction distribution coefficient of 0.2. Under these conditions the effect of radiation is to reduce iodine to the iodide which is non-volatile. Therefore, the bulk of iodine may show up in either the reactor dump tank or the condensate from the recombiner condenser, depending on how rapidly valence state reduction and mass transfer takes place as the temperature of the letdown stream is lowered. Present data indicate that the condensate would contain the bulk of

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the iodine. Isolation of iodine from such a water stream by distillation should be practicable. Separation from the reactor fuel in the dump tank probably would require fixation on silver. The actual distribution of iodine between these two portions of the HRT system will be studied before a means of final isolation of the iodine is developed.

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