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SUBJECT: Status and Future Program of Homogeneous Reactor
Fuel Processing Studies

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ABSTRACT

The behavior of insoluble corrosion products in the HRT is generally understood and studies of the removal of these solids by hydroclones can logically be terminated after the effect of higher processing rates by the multiple hydroclone has been determined. Chemical descaling may be required to supplement solids removal by hydroclones. Laboratory studies to find suitable reagents will be continued in conjunction with decontamination work presently in progress.

Rare earth solubility levels and thus poison fraction from this group will be measured after the addition of significant quantities of four important elements has minimized analytical detection problems. The role of the tellurium precursor in the interpretation of iodine behavior will be examined extensively in the present run in an effort to resolve previous discrepancies. Studies of iodine behavior can be continued after shutdown of the hydroclone system if required.

An electrolytic process for removal of nickel from fuel solution has been developed through the laboratory and engineering scale except for the design and testing of a cell suitable for radioactive environments.

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With termination of all homogeneous reactor fuel processing studies scheduled within the first few months of FY-60, the present status of the development program and goals still to be achieved have been reviewed and are summarized here.

Insoluble Corrosion Products

Performance of Single Hydroclone. Prior to operation of the HRT-CP hydroclone system, it became apparent that competing mechanisms for solids removal would seriously limit the fraction of corrosion product solids removed by a hydroclone system. In 2670 hours' operating time with the HRT, 2.2 kg of corrosion products have been collected, which is only about 10% of those produced in the core system. The over-all average removal rate of 0.8 g/hr (compared with a normal corrosion rate of ~ 3 g/hr) is augmented considerably by high removal rates in the first 200 hours of reactor runs. Rates initially have been as high as 2.6 g/hr, but under all conditions, have dropped to and remained consistently at 0.3 g/hr after 250 hours. The only factor which has consistently changed removal rates is a reactor shutdown and start-up. Two periods of high corrosion rate produced substantial quantities of solids above what is normally expected and significantly the solids removal rate was not higher during one of these periods than under normal circumstances. Other variables such as reactor power and total reactor solids inventory do not appear to have a marked effect on removal rates either.

From the chemical composition of solids collected, it is clear that the solids are largely those from previous runs which have been resuspended. From removal rates and known hydroclone efficiencies the long-term equilibrium circulating solids concentration in the reactor is only about 2 ppm, corresponding to a total circulating solids inventory of only 1 g, and the maximum concentration at the beginning of a run is no more than an order of magnitude higher. This concentration of solids can be of no consequence to reactor operations, but the long-term buildup or accumulation in such places as the reactor core or small lines may cause difficulties as yet uncovered. Since normal corrosion rates are a factor of 3 higher than average removal rates and 10 higher than long-term equilibrium rates, it does not appear that the present system can in the foreseeable future, if ever, maintain an equilibrium solids level in the reactor.

Solids Removal by the Multiclone. Performance of the hydroclone loop to-date has indicated that the circulating solids concentration is not greatly affected by operation of the single hydroclone. From this it follows that solids removal would be proportional to processing rate and removal rates could be increased to equal production rates by faster processing. A multiple hydroclone containing 13 hydroclones in parallel was designed, fabricated, and installed prior to the present run (Reactor Run 20) and will test this theory. Data from operation of this multiclone will aid in interpretation of present information, and should make it possible to predict solids removal rates in other systems. Removal rates

with the multiclone are predicted to be 3 to 4 times as high as with the original single clone. The removal rates will not be directly proportional to the number of hydroclones since the head available across the heat exchanger is only 70 ft and nearly half of this is taken by line losses to the hydroclone, compared with the 100-ft head used with the single hydroclone. In addition, some of the solids (estimated at 50%) removed by the multiclone will be lost by the single clone in Cell C which acts as the final collector.

Assuming reasonably consistent data is obtained from the present run the experimental function of the HRT chemical plant will have been logically concluded. If the predicted multiclone performance is achieved, removal rates will equal production rates and the solids inventory should be held constant, in which case it may prove desirable to continue operation of the multiclone system.

If solids removal rates are not increased markedly with the multiclone, the hydroclone system as presently envisioned will have been shown completely infeasible for removing corrosion product solids from homogeneous reactors. While some means of controlling corrosion product particle size and characteristics to enhance removal by hydroclones might be developed, at present no such means is known.

Solids Material Balance and Descaling Studies. Scale on corrosion specimens examined to-date indicate a substantial fraction of the corrosion products are deposited more or less uniformly on all surfaces outside the core of the high-pressure system. In the heat exchanger some lowering of the heat transfer coefficient has been noted and eventually may necessitate chemical descaling to restore performance. Results of laboratory and loop descaling work to-date have been indeterminate. Scales have been removed successfully, but the solutions are rather corrosive and the question of whether H_2 pickup is excessive in the reducing atmosphere of most of the successful descaling reagents has not been resolved. These studies should be continued until a suitable solution and operating conditions have been found. A successful descaling procedure could supplement solids removal by hydroclones and could conceivably replace it completely. At normal corrosion rates, a homogeneous reactor could certainly operate one or two years with no solids removal without significant worries from scale buildup. In addition any successful decontamination for cell maintenance or recovery of equipment depends initially on scale removal, and the same procedures would be applicable.

The solids material balance in the reactor will be refined as additional information becomes available. Information from corrosion specimens will adequately determine scale thickness and solids inventories in the high-pressure system. At present the biggest gap in the balance is the quantity of solids in the dump tanks. A method suggested for measuring this quantity is to dissolve the solids from the dump tanks during the shutdown for core screen removal using one of the descaling reagents. The reagent probably will dissolve only iron and chromium oxides, but the

quantity of zirconium could be determined from the composition of a solids sample removed from the dump tanks. If a suitable reagent is found, it should be tested on the core mockup at Y-12 prior to addition to the reactor.

Fission Product Behavior

The majority of the long-lived radioactive isotopes, with the exception of cesium, are relatively insoluble. A large group, including Zr-Nb, Ru, and Te, are very insoluble with only a fraction of one percent circulating in the fuel stream and the remainder associating with the corrosion product solids.

Iodine. Laboratory and loop studies have shown that iodine is easily volatilized from HRT fuel solutions. On the basis of these studies, an iodine trap was installed in the reactor low-pressure system to remove iodine let-down from the core. The primary functions of iodine removal on the HRT were to minimize biological hazards and to prevent poisoning of the low-pressure recombiner catalyst. In power reactors, iodine removal on a 45-minute processing cycle would effectively control xenon poisoning.

Examination of the iodine data obtained during HRT operation leads to two opposing conclusions. The quantitative measurement of the amount of iodine present in the fuel solution of the HRT indicates that iodine is being effectively removed from the fuel solution on about a one- to two-hour processing cycle time equivalent to the let-down rate. However, the age of the iodine found in solution, as determined by the activity ratio of I^{133}/I^{131} , indicates that the processing cycle time for iodine removal is more nearly twenty-four hours. Several possible explanations for these results must be examined to explain the discrepancy. The uncertainty in the branching ratio of the tellurium precursors as well as the chemical behavior of tellurium in the reactor and in the samples after isolation from the reactor but before chemical separation for activity analysis can lead to false conclusions. The role of tellurium in the iodine picture will be studied extensively in the present run.

Adsorption of iodine on corrosion product was noted in limited laboratory studies and this phenomena should be pursued further both in the laboratory and with HRT solids. Sizeable quantities of silver are present in the reactor fuel and as solids associated with corrosion products. The effect this might have on holdup of iodine in the circulating system should be determined in laboratory studies.

Rare Earths. Very limited data from radiochemical analyses indicate the important rare earth poison group may be less soluble than anticipated, holding the total poisoning from this group to no more than 1.5% in a large power reactor. Concentration levels from normal fission product buildup are not sufficiently high to check this data by more direct analyses. The gross addition of four major rare earths to be made in the

present run should minimize analytical problems and permit definite establishment of their behavior in the reactor. In this program solubility levels will be established as a function of temperature and power level and the location of precipitated elements will be determined if possible.

Gaseous Fission Products. Performance of the HRT charcoal adsorber beds has demonstrated the capacity of the beds is more than adequate. Supporting laboratory studies have fully defined the variables affecting bed performance and have developed information about a large number of other adsorbents of potential value in large power reactor systems. Beds for large systems have not been designed, but sufficient information has been obtained to permit an adequate design.

Electrolytic Nickel Removal

Since, at present, purge rates required to maintain suitable soluble contaminant levels in the reactor fuel solution are set by the buildup of nickel from stainless steel corrosion, a separate nickel removal system, if reliable and cheap, could reduce over-all processing costs. Laboratory studies of the electrolytic removal of nickel and manganese from uranyl sulfate-sulfuric acid solutions have shown that essentially all of the nickel and manganese, along with the copper present in HRT fuel solution, can be removed from such solutions when mercury is used as the cathode. Pickup of mercury by the solution has been below analytical detection limits. With solid metal cathodes no manganese and only a small amount of nickel can be removed. The behavior of fission products in the fuel during electrolysis was not studied and (at present) there are no plans to continue this phase of the program. For a given cell the removal is more rapid and more complete in D_2O than in H_2O . Regeneration of the mercury for cathode use can be accomplished by treatment with various reagents, the best of which appears to be 1 M nitric acid containing 1.5% hydrogen peroxide or by a slurry of mercurous sulfate or nitrate in the corresponding acid of 1 M strength. During electrolysis uranium six is reduced to uranium four and the rate of nickel removal appears to be affected by the valence state distribution of the uranium. Reoxidation of the uranium can best be accomplished with an oxygen-ozone mixture at $25^{\circ}C$.

Procedures for the electrolysis and for cathode regeneration were demonstrated with HRT scale equipment. These tests were in a glass-lined cell with organic insulating materials to eliminate excessive stray currents and electrolytic corrosion. Design of a cell acceptable for a high radiation field, and appropriate demonstration of the design will not be done at this time.

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