OAK RIDGE NATIONAL LABORATORY

Operated by
UNION CARBIDE NUCLEAR COMPANY
Division of Union Carbide Corporation

Post Office Box X
Oak Ridge, Tennessee

External Transmittal
Authorized

ORNL
CENTRAL FILES NUMBER

58-5-33

DATE: May 31, 1958

SUBJECT: Aqueous Homogeneous Reactor Fuel Processing--
The Behavior of Insoluble Corrosion and Fission Products

TO: F. L. Culler, Jr. (To be presented at the American Chemical
Society's Nuclear Technology Symposium, Boston, April 5-10, 1959)

FROM: P. A. Haas

COPY NO. 49

ABSTRACT

Information is presented from studies with materials and conditions simulating those expected in an aqueous homogeneous reactor for the formation of insoluble corrosion and fission products in aqueous UO_2SO_4 solutions used as a reactor fuel. Sulfate salts which become insoluble as the temperature increases deposited preferentially and reversibly on hot walls. Oxides from hydrolysis of sulfate salts deposit on any surfaces while insoluble corrosion products released into the solution show variable degrees of circulation.

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission.

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights, or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

CONTENTS

	<u>Page</u>
1.0 Summary	3
2.0 Introduction	3
3.0 Methods of Study	6
3.1 Sulfate Salts with Inverse Temperature Dependent Solubility	6
3.2 Insoluble Salts (Sulfates and Oxides) Formed in the Solution	7
3.3 Preformed (Corrosion Product) Oxides	7
4.0 Results	11
4.1 Sulfate Salts with Inverse Temperature Dependent Solubility	11
4.2 Insoluble Salt (Sulfates and Oxides) Formed in Solution	21
4.3 Preformed (Corrosion Product) Oxides	24
5.0 Conclusions	32
6.0 References	33

1.0 SUMMARY

Information is presented from studies with materials and conditions simulating those expected in an aqueous homogeneous reactor for formation of insoluble corrosion and fission products in aqueous UO_2SO_4 solution used as a reactor fuel. The behavior of rare earth sulfates, $\text{Zr}(\text{SO}_4)_2$, ZrO_2 , iron oxides, chromium oxides, and mixtures of these were studied with various types of laboratory equipment and experimental loops in 0.02 to 0.04 M UO_2SO_4 at room temperature to 325°C. Sulfate salts which become more insoluble without decomposing as the temperature increases deposit preferentially and reversibly on "hot walls" which have surface temperatures above the solution temperature. When sulfate salts hydrolyzed in the UO_2SO_4 solution circulating in a loop, the resulting insoluble oxides deposit on the available surfaces or circulate for short periods only. Corrosion product oxides released into the circulating fuel solution as solid particles circulate to a much greater extent than sulfate salts hydrolyzed to oxides. However, the characteristics and behavior of corrosion product solids in a homogeneous reactor fuel system have not been definitely established. Results showed that geometry (including the type of surface, the surface to volume ratio, the wall to fluid temperature differences, and the existence of dead end or no flow regions) is a controlling factor when comparing different systems.

2.0 INTRODUCTION

Insoluble materials are formed in UO_2SO_4 solutions used at 200 to 300°C as fuel for an aqueous homogeneous reactor. The sources are the fission products and corrosion of the container walls. Some of the insoluble fission products are serious nuclear poisons. Circulation of even a dilute slurry introduces the problems of avoiding mechanical effects such as fouling of heat transfer surfaces, wear or erosion of pump bearings, and valve failures.

The characteristics and behavior of these insoluble materials were studied with two major objectives. One objective was to devise a successful fuel processing method based on liquid-solid separation. For the Homogeneous Reactor Test (HRT), the removal of 56 per cent of the fission products as insoluble material and 30 per cent as rare gases would result in removal of at

least 86% of the fission products and would only leave <2 per cent as soluble salts and 12 per cent of undetermined behavior. The other objective was to evaluate as completely as possible the characteristics and behavior of these materials in order to determine their effects on the operation of the nuclear reactor.

The behavior and characteristics of these materials are determined by the temperatures and pressures at which they are observed. For aqueous homogeneous reactors at the Oak Ridge National Laboratory, the conditions of interest would be 3 to 10 g U/Kg D_2O as UO_2SO_4 solution with excess SO_4^{--} as H_2SO_4 and with an O_2 overpressure at 200 to 300°C. The solubilities and compositions of the fission and corrosion products were determined by small scale studies in laboratory equipment. Dynamic studies were in loops with canned rotor pumps for circulation. A processing pilot plant operating with the HRT (Homogeneous Reactor Test) supplied information from a more complex system both from tests during checkout operating and from operation with the reactor.

The insoluble corrosion and fission products in the UO_2SO_4 solution fuel have three distinct modes of behavior depending on their type and their source. Each type was studied separately and in combination with the other types. The behavior differences are still apparent in mixtures of types although a small amount of one type will tend to follow the behavior of the predominant material.

The fission products will first appear as positive ions; therefore the initial at-rest status of cations can be considered to be dissociated sulfate salts. Corrosion products form below an oxide film; circulating insoluble corrosion products are probably released as insoluble particles from the surface of the film. The predicted formation rates for the HRT at design power were about 50 g/week of insoluble fission product salts and 350 g/week of corrosion product oxides. Solubilities of fission products can be expressed in terms of MWD for various classes of cations (see Table I).

Sulfate salts which become more insoluble without decomposing as the temperature increases deposit preferentially and reversibly on "hot walls" which have surface temperatures above the solution temperature. The major salts of this type in the UO_2SO_4 fuel solution will be the rare earth fission

products since their solubility decreases as the temperature increases. The rare earths including Nd, Sm, and Ce are a major part of the fission product poisoning and 28 wt per cent of the total fission products.

Table I. Insoluble Major Fission Products in the HRT (1)

Chemical Group or Element	Rate of Production (mg/Kg D ₂ O·MWD)	Solubility (mg/Kg D ₂ O)	Time to Saturation at 300°C (MWD)
Rare Earths	0.67	85	127
Alkaline earths	0.15	10	67
Zirconium	0.27	< 1	< 4
Ru, Rh, Pd	0.16	< 5	< 31

When sulfate salts are hydrolyzed in UO₂SO₄ fuel solution circulating in a loop, the resulting insoluble oxides are deposited on the available surfaces or circulate for short periods only. This is distinctly different from the behavior of oxides which appear in circulation as an insoluble slurry. Therefore the addition of soluble sulfate salts does not give representative results for corrosion product behavior. The sulfate salts available for hydrolyses are a fraction of the fission products; therefore, the amount of this type of insoluble material is the smallest of the three types of solids studied. Zirconium is the major fission product which would hydrolyze to give an insoluble oxide, and it amounts to about 11 wt per cent of the fission products. The alkaline earth fission products and the Ru-Rh-Pd group are about 6 and 7 wt per cent, respectively, of the total fission products and will also form insoluble compounds.

The oxides of Zr, Fe, and Cr from corrosion of the fuel system walls are expected to be over 80 per cent of the insoluble salts formed in the HRT fuel system. They would probably be over 50 per cent of the insoluble salts for any aqueous homogeneous reactor operating at over 200°C in a stainless steel system. The behavior and characteristics of the corrosion products become of interest whenever they leave the site of formation and

are transported by the circulating fuel fluid. The Fe, Cr, and Zr are probably released as solid particles from the oxide films on the metal surfaces. The nickel appears as a soluble sulfate and does not precipitate for the normally anticipated amounts of corrosion.

Ideas and experimental data contributed by a number of people have been incorporated into this paper. Laboratory studies by R. A. McNees, loop studies by R. W. Horton, and pilot plant operation directed by W. D. Burch merit particular acknowledgement.

3.0 METHODS OF STUDY

Varying methods and procedures were necessary due to the differences in behavior between the three characteristic types of insoluble materials studied.

3.1 Sulfate Salts with Inverse Temperature Dependent Solubility

The behavior of both individual rare earth sulfates and mixtures of salts were studied in the laboratory and in dynamic loops. The laboratory studies were chiefly by optical observation of the solutions in thermostated quartz capsules. The loop studies were mostly with $\text{Nd}_2(\text{SO}_4)_3$ as a representative material since this salt and Nd-147 tracer were easily available. The sensitivity of tracer analyses were necessary for the low concentrations at 250-325°C. Mixed rare earths and Ce-141 tracer were used in loop studies to compare mixtures with pure $\text{Nd}_2(\text{SO}_4)_3$. Other pure rare earths were used in laboratory studies to make more detailed comparisons.

Obtaining representative samples and addition of the rare earth salts were major problems during all loop studies. Since these precipitates redissolved upon cooling, separation of the solution and precipitate at loop temperature would be necessary if the precipitate is to be examined at lower temperatures. Use of removable bombs in valved by-pass lines with multiple displacements of the bomb contents was found to be the only completely dependable loop sampling procedure and was also an effective feed addition method. Feed solution was also added by use of Lapp Pulsafeeder metering pumps. None of a variety of sampling methods involving discharge of a fraction of the loop volume gave consistent and reproducible results.

3.2 Insoluble Salts (Sulfates and Oxides) Formed in the Solution

This type of material was represented by hydrolysis of $\text{Zr}(\text{SO}_4)_2$ to give ZrO_2 in the loop. Solubilities were determined in the laboratory. Mixed sulfate solutions of Zr, Fe, and Cr were hydrolyzed to the oxides in circulating UO_2SO_4 solutions for some tests. The $\text{Zr}(\text{SO}_4)_2$ is relatively soluble in $0.04 \text{ M } \text{UO}_2\text{SO}_4$ - $0.02 \text{ M } \text{H}_2\text{SO}_4$ at room temperature. For some experiments, a loop was started with $\text{Zr}(\text{SO}_4)_2$ in solution at room temperature and was gradually heated to the operating temperature of 200°C to 300°C with periodic sampling. A more common procedure was to add a concentrated solution of $\text{Zr}(\text{SO}_4)_2$ in $0.04 \text{ M } \text{UO}_2\text{SO}_4$ to a loop operating at temperature. One method of addition was by use of a Lapp Pulsafeeder pump. Another was to insert a bomb containing the Zr_2SO_4 into a valved-off by-pass and then to open the valves to permit circulation through the bomb.

Sampling problems were the same as for preformed corrosion product oxides (see Section 3.3) as far as obtaining the concentrations of ZrO_2 was concerned. Since insoluble Zr did not redissolve, samples for soluble Zr concentrations were easily obtained. The concentrations of circulating solids were actually so low that consistent measurements were never obtained.

The zirconium concentrations were measured by use of scintillation counting of Zr-95 tracer. Chemical analyses and weight measurements were used for check analyses and for some special measurements. The decay of the tracer and the contribution of the Nb-95 required careful calibrations and calculations to avoid errors. The Nb-95 disappeared preferentially when traced Zr was first added to a loop.

3.3 Preformed (Corrosion Product) Oxides

The experimental methods for corrosion product oxides were largely dictated by the need for minimizing the limitations on the validity of the results. These limitations were due to features of the experimental loop facilities (see Figure 1), the experimental procedures, and the synthetic materials used to represent the corrosion products. None of the experimental facilities used give reactor values for all variables (see Table II). Three important variables which were only partially duplicated were the system geometry, including flow velocities and surface to volume ratios, the system temperature, and the difference between fluid and wall temperatures.

Figure 1. (a) A-loop, (b) B-2 loop, and (c) glass loop as used in ZrO_2 behavior studies.

Table II. Comparison of Experimental Facilities

Property Compared	Units	Value of Property for:						
		HRT	HRT Mock-Up	Loop A	Loop B-2	HRT-CPP Test	Glass Loop	Loop P-1
Liquid Charge	Kg H ₂ O	410	75	1.1	10	31	0.65	11
Surface	ft ²	600	52	3.3	7.2	16.7	1.70	10.4
Volume/Surface	ft ³ /ft ²	.03	.07	.015	.06	.08	.013	.05
Maximum Temperature	°C	300	300	320	300	280	90	270
Typical Flow* Velocities	ft/sec	11-19	10-20	3-5	5-22	6-20	3-6	6
Relative Magnitude of Hot Walls	---	Negligible	Moderate	Large	Small	Large	Small	None

* An average velocity for the major volumes of the system.

The adequacy of operating procedures was determined by the ability to give known starting conditions, to obtain representative samples, and to obtain consistent analytical results. Circulation through bombs was the only satisfactory method of obtaining samples or of adding insoluble material to loops at high temperature and pressure. Samples taken by various procedures other than circulation through bombs were frequently found to be completely and unpredictably unrepresentative. Many conventional analytical techniques, including gravimetric, were not practical for the 1 to 1000 ppm range of concentrations of insoluble materials. Tracer and light transmission analyses were very useful, but activity and size distribution determinations respectively were required along with independent check methods of analysis for comparison purposes.

The natural fission and corrosion products in a reactor would be very complex mixtures; therefore, single compounds or simple mixtures were substituted to simplify the chemical analyses and the interpretation of results. The initial procedure selected for studying these corrosion product oxides was to hydrolyze sulfate salts in the circulating loop solution. The oxides circulating after hydrolyses was complete were expected to behave as material released from the surface of corrosion films. The small fractions (less than 10 per cent) of the oxides which circulated after hydrolyses indicated that both the results and this method of formation were of doubtful validity. To check the above conclusion, a slurry of ZrO_2 was added to loop A for conditions otherwise comparable to those previously used for a test with $\text{Zr}(\text{SO}_4)_2$ addition (see Table III).

Table III. Comparison of $\text{Zr}(\text{SO}_4)_2$ and ZrO_2 Behavior

Results	$\text{Zr}(\text{SO}_4)_2$ Addition Test	ZrO_2 Addition Test
Zr circulating (%)	< 1%	7%*
Zr recovered (%)	47%	99%
Zr in hydroclone pot (%)	15%	87%

* This would be approximately 60% if the ZrO_2 removed by the hydroclone were subtracted from the amount of feed Zr.

Most of the solids behavior studies were made with preformed oxides which may or may not have been representative substitutes for reactor corrosion products. The preformed oxides were prepared by precipitation with ammonium hydroxide from zirconium or mixed zirconium-iron-chromium sulfate solutions at atmospheric pressure. The hydrated oxides were digested, filtered, washed, slurried up in $.04 \text{ M } \text{UO}_2\text{SO}_4$, and digested in an autoclave at 300°C with O_2 overpressure. This gave particles with mean diameters (based on wt %) of 0.05 to 1 micron. Some corrosion loops have yielded scale like material with much larger particle diameters. Some laboratory bomb studies have shown marked differences in particle characteristics above 260°C depending on the composition (2). When concentrations were to be determined from γ activity counts, Zr-95 was added before precipitation or the preformed ZrO_2 was irradiated in a nuclear reactor before use.

4.0 RESULTS

Experimental results are presented which are typical of the behavior of the three characteristic types of insoluble material. Two major limitations should be noted and considered throughout the following discussion. One is that all studies prior to critical operation of the HRT were in H_2O without the presence of radiation or radiolytic gas. Preliminary laboratory measurements indicate rare earth solubilities in D_2O at 27°C to be 50 to 60 per cent of those in H_2O for similar conditions. The other is that results reported from the HRT Chemical Processing Plant are for low degrees of uranium burnup compared to those required for power reactors.

4.1 Sulfate Salts with Inverse, Temperature Dependent Solubility

Laboratory solubility data were obtained for a number of rare earth sulfate salts and mixtures of salts (see Table IV)(see Figures 2 and 3). The solubility of a specific salt is reduced by the presence of other rare earths. The concentrations circulating in loops were found to be essentially solubility values for the loop conditions. A reversible temperature-concentration curve of this type was obtained in the absence of hot walls (see Figure 4).

Table IV. Solubility of Rare Earth Sulfates in UO_2SO_4 Solution

Conditions: Noncirculating laboratory tests

0.02 M UO_2SO_4

0.005 M H_2SO_4

280°C

Salt	Solubility in mg/Kg H_2O
$\text{La}_2(\text{SO}_4)_3$	10
$\text{Ce}_2(\text{SO}_4)_3$	50
$\text{Nd}_2(\text{SO}_4)_3$	110
$\text{Pr}_2(\text{SO}_4)_3$	170
$\text{Y}_2(\text{SO}_4)_3$	240
$\text{Sm}_2(\text{SO}_4)_3$	420

The reversibility of Nd concentration was demonstrated for twenty-five temperature cycles in a loop (see Figure 5). Recovery of Nd was excellent for most of these tests (85-110%). The final rare earth sulfate solubilities (see Figure 6) were reasonably reproducible and consistent. Much lower values were obtained from earlier measurements due to unrecognized sampling and hot wall effects.

The insoluble $\text{Nd}_2(\text{SO}_4)_3$ deposited out on loop walls very rapidly with a pronounced preference for walls with temperatures above the solution temperature. During one loop test designed to give a high heat flux in the preheater to the pressurizer, the preheater collected 99% of the Nd added to the loop while a hydroclone after the preheater collected 1/2%. Even when corrosion product oxides were present, the $\text{Nd}_2(\text{SO}_4)_3$ deposited preferentially on hot surfaces and formed separate crystals of precipitated material. The solids were redissolved completely and the effects on heat transfer were completely reversed by dropping the temperature of the circulating solution (see Figure 5).

ORNL-LR-DWG. 2-A
UNCLASSIFIED

SOLUBILITY OF $\text{Nd}_2(\text{SO}_4)_3$ IN $0.02 \text{ M } \text{UO}_2\text{SO}_4$,
 $0.005 \text{ M } \text{H}_2\text{SO}_4$

Figure 2

ORNL-LR-DWG. 469
UNCLASSIFIED

SOLUBILITY OF MIXED RARE EARTH SULFATES IN
0.02M UO_2SO_4 , 0.005M H_2SO_4 SOLUTION.

(48 % Ce, 24 % La, 19 % Nd, 6 % Pr, 2 % Sm, 1 % others)

Figure 3

Figure 4.
Neodymium Sulfate Concentrations vs Fuel Temperature in Loop B₂

Figure 5

Figure 6. Solubilities of Rare Earth Sulfates in UO_2SO_4 Solutions.

The rates of precipitation and re-solution were normally too fast for detection in dynamic loop experiments. When the $\text{Nd}_2(\text{SO}_4)_3$ concentration exceeded the solubility gradually either by slow additions or temperature increases, the amount circulating showed an excess over the solubility for as long as four hours after which the amount circulating dropped back to and stayed at the solubility value for the conditions in the loop. Efforts to obtain crystals of $\text{Nd}_2(\text{SO}_4)_3$ on filters kept at loop temperature and pressure were not successful. Any flashing reduced the temperature and dissolved the $\text{Nd}_2(\text{SO}_4)_3$ while temperatures above the loop temperature caused deposition in the filter. The deposits on the preheater hot walls were removed and examined after draining the loop while maintaining the operating temperature and pressure. Some deposits completely plugged the preheater cross-section for flow.

The results with $\text{Nd}_2(\text{SO}_4)_3$ are reasonably representative of the behavior of the other rare earth sulfates; this fact was indicated by extensive laboratory and limited loop tests. As previously mentioned, the actual solubilities are greatly reduced by the presence of other rare earths. Various rare earths may co-precipitate with other rare earths, or, in some cases, with UO_2SO_4 . During loop studies with mixed rare earth sulfates, the concentration of $\text{Nd}_2(\text{SO}_4)_3$ was less than one-third of the Nd concentrations for studies during which $\text{Nd}_2(\text{SO}_4)_3$ was the only rare earth added (see Figure 7)(see Table V). Concentrations of Nd and Ce calculated from Nd-147 and Ce-144 activities as determined by selective shielding counting were checked by separation by decay curves. The composition by weight per cent of the sulfate salts was 48% cerium, 24% lanthanum, 18% neodymium, 6% praseodymium, 2% samarium, and the remainder other rare earths. The tracer activity in the feed to the loop was about 30% 11.6 day Nd-147 and 70% 280 day Ce-144. When the loop was cooled down at the end of the run, 30% of the Ce and 75% of the Nd tracer (or 45% of the total tracer activity) were in the solution drained from the loop. About 5% and 20% of the tracers were removed by dilute H_2SO_4 and H_2O_2 , 0.1 N H_2SO_4 washes of the loop, respectively.

The insoluble fission product sulfates will be a major fraction of the nuclear poisoning and radioactivity in the HRT fuel solution, but will be less than 5 per cent of the total insoluble fission and corrosion products.

Figure 7. Concentration of Nd and Ce in Loop B-2 After Addition of Mixed Rare Earths.

Table V. Loop B-2 Concentrations of Nd and Ce
In the Presence of Mixed Rare Earths

Conditions: 11 g uranium/kg H_2O , 0.015 N H_2SO_4

Operation with and without hot walls to $\pm 2^\circ C$.

Rare Earth Concentrations: 5 g/kg H_2O of mixed rare earth sulfates, or
pure $Nd_2(SO_4)_3$ only.

Temperature ($^\circ C$)	Concentrations in presence of mixed rare earth sulfates (mg sulfate salt/kg H_2O)		Nd only rare earth present (mg $Nd_2(SO_4)_3$ /kg H_2O)
	$Nd_2(SO_4)_3$	$Ce_2(SO_4)_3$	
200	200	250-400	1200
280	50	30-35	180

Future reactor designs may increase the fraction of the insoluble material which is fission products, but the amount of corrosion products will probably always be at least several times the amount of fission products.

Radiochemical analyses of the HRT fuel solution agree with the observed non-radiative behavior of rare earths. Accumulation of Nd-147 and Y-91 in the circulating solution during initial operation would correspond to the behavior of unsaturated solutions. The drop from 100% circulating to 40% circulating in later tests (3) would correspond to deposition after the fuel solution became saturated with Nd and Y. The chemical processing plant's liquid-solid separator only collected a small fraction of the Nd and Y which disappeared. However, the concentration factors increased from one for both nuclides to 8.0 for Y-91 and 3.5 for Nd-147 at the times at which the percentages in circulation dropped.

4.2 Insoluble Salts (Sulfates and Oxides) Formed in Solution

Results typical of the addition of soluble Zr or Fe sulfates to precipitate oxides in the loop were 3, 4, 8, and 0.1 per cent in circulation and 110, 50, 49, and 47 per cent of the material added recovered. Two loops were disassembled and inspected after the addition of large amounts of $\text{Zr}(\text{SO}_4)_2$. Both layers of hard dense scale 0.002 to 0.006 in. thick over essentially all of the loop surfaces (see Figure 8). Where the additions were by use of a high pressure metering pump, the scale was thickest at the point of feed addition and became thinner downstream. However, all surfaces including those of relatively stagnant sample and instrument taps showed deposits of ZrO_2 .

Although the amounts of hydrolyzed oxides circulating were small percentages of the amounts of sulfate added, major amounts (16, 70, 45, and 65 per cent) were collected by the hydroclones in the loop systems. The mean apparent Stokes diameter on a weight percentage basis of ZrO_2 collected by a hydroclone was about 1 micron. The lowest percentage collection listed was during a long term continuous addition tests with low circulating solids concentration at all times. At a 100 mg/liter concentration of 1 micron diameter, the surface area of the circulating solids will approximately equal the wall area of the experimental loops. Since the solids are throughout the turbulently flowing fuel solution, they could effectively compete with the walls for collecting the freshly precipitated oxides from sulfate salts. This type of effect could explain most of the variations in material balances and fractions collected by the hydroclones during tests with $\text{Zr}(\text{SO}_4)_2$ addition.

When a loop containing $\text{Zr}(\text{SO}_4)_2$ was brought up to and held at a steady state temperature, the concentration of zirconium remaining in solution quickly dropped to a constant value. These values were not temperature reversible and do not represent solubilities of the type found for rare earth sulfates. Also samples were not filtered unless they contained visible solids. The values for a variety of conditions show a consistent temperature dependence (see Figure 9). The effects of UO_2SO_4 and H_2SO_4 concentrations are not apparent since the experiments were not conducted to study these variables.

UNCLASSIFIED
PHOTO 18995

Figure 8. Pump Impeller and Thermal Barrier.

Figure 9. Concentrations of Zr in UO_2SO_4 Solutions Circulating in Loops.

The behavior of fission products for which the sulfate salts are insoluble at all temperatures (alkaline earths) was not studied except for the determination of solubilities. These materials are expected to behave similarly to ZrO_2 in that precipitates will form and immediately attach themselves to all available surfaces. Solubilities of the relatively insoluble fission products are expected to be 10 mg/Kg H_2O for the alkaline earths and < 5 mg/Kg H_2O for Ru, Rh, and Pd.

Radioactivity analyses for Zr-95, Ru-103, and Sr-89 in the HRT confirm the differences in behavior of the insoluble fission product sulfates and oxides as compared to the corrosion products. After the fission product solubilities are reached, usually less than one per cent of the insoluble sulfates and oxides are collected by the chemical processing plant. Material balances calculated for early operation of the HRT chemical processing plant (3) indicate from 0.04 to 3.5 per cent collected for Zr-95, Ru-103, and Sr-89 (see Table VI). From .02 to .24 per cent of the Zr-95 and Ru-103 were circulating in the reactor system while 40 to 59 per cent of the more soluble Sr-89 and 93-120 per cent of the completely soluble Cs-137 were circulating. The removal of Zr and Ru was proportional to the removal rate of corrosion product solids. However, the fraction of these fission products collected appears to be 1/10 to 1/50 of the fraction of corrosion products collected. One-half ppm or 0.5 mg/Kg H_2O concentration of 1 micron diameter corrosion products would have a surface in the HRT of about 1 per cent of the wall surface of the fuel system. Thus equal deposition on all surfaces including the corrosion product particles would agree with the observed collection rates for insoluble fission products.

4.3 Preformed (Corrosion Product) Oxides

Results have shown that geometry including the type of surface, the surface to volume ratio, the wall to fluid temperature differences, and the existence of dead end or no flow regions is a controlling factor when comparing different systems. Because of the controlling geometry effects, variations of temperature, flow rate, and concentration did not give consistent results for the initial tests with preformed ZrO_2 . Later studies with more carefully controlled conditions showed consistent variations in the amount and rate of ZrO_2 deposition on coupons with Reynolds number

Table VI. HRT Fission Product Material Balances*

Basis: Calculated activities from fission yields and reactor power history.

Quantity	Run No.	% of calculated activities for nuclides:			
		Zr-95	Ru-103	Sr-89	Cs-137
Removed by chemical processing plant	16-2	0.51	0.55	0.23	0.54
	16-3	0.26	0.19	0.39	0.63
	17-4	3.5	0.04	0.65	1.3
	17-5	0.65	0.47	0.60	1.0
	17-6	0.22	0.13	0.39	0.83
Circulating in reactor	16-2	0.20	0.14	49	99
	16-3	0.24	0.09	59	87
	17-4	0.10	0.13	40	120
	17-5	0.04	0.02	46	110
	17-6	0.03	0.03	40	93

* Reported by W. D. Burch, et al (3).

changes caused by flow rate or temperature changes (see Figure 10)(4). Higher initial ZrO_2 concentrations gave somewhat higher, but not directly proportional concentrations throughout the test periods. Location of ZrO_2 in the circulating pump at the end of experimental studies (5) and location of corrosion products in relatively stagnant areas of the HRT Mock-up or of REED corrosion loops has confirmed the tendencies of these regions to collect solids.

Results for successive additions of ZrO_2 to an operating system (loop A) were compared to results for a single addition of the same total amount (5). The successive additions resulted in concentration versus time curves having successively flatter slopes and higher steady state concentrations (see Figure 11). A test with continuous addition of traced ZrO_2 to loop B-2 for three periods totaling over 250 hours and essentially continuous hydroclone operation was

UNCLASSIFIED
ORNL-LR-DWG 31153

Figure 10. Concentration of ZrO₂ as a Function of Time with Varying Temperatures in (a) and (b) A-loop and (c) B-2 loop. N_{Re} based on flow through 1/2-in.-dia pipe in A-loop and through 1 1/2-in.-dia pipe in B-2 loop. C_0 based on volume of solids suspension added.

Figure 11.
Suspended Solids vs Time for Successive Additions of Loop to A-Loop

made to determine the steady state loop and hydroclone underflow receiver concentrations. Average steady state concentrations during the continuous ZrO_2 addition were about 380 mg/kg H_2O of solids in the loop and 2000 mg/kg H_2O in the underflow receiver (6). At steady state, the ZrO_2 added was collected in the underflow receiver at 50% of the addition rate; the other 50% disappeared from circulation and was not recovered by draining and flushing the loop.

Tests of limited scope with preformed oxides were made with the relatively complicated geometries of the HRT-CPP and the HRT Mock-up for comparison with results from simpler loop systems (7). Results of the most typical tests in each system are most easily compared by tabulation (see Table VII). The parameters for these systems have also been tabulated (see Table II). The HRT-CPP studies clearly showed sudden sharp increases in circulating solids concentrations (7); similar changes were observed to a lesser degree in loop A and in other studies. The reappearance of solids often followed temperature changes, but some reappearances occurred with no visible changes in experimental conditions.

Higher corrosion rates for zirconium and stainless steel under radiation, as compared to non-radiative conditions, indicates changes in the oxide film on the metals and thus in the corrosion products released to the circulating solution. Settled corrosion product oxides recovered from corrosion test loops have complicated histories and their properties may not be characteristic of what is initially released from the corrosion sites. General indications are that the loop corrosion products have larger, scale-like particles with higher settling rates as compared to the preformed oxides used for development studies. Some properties found for preformed oxides and some other materials examined during experimental studies are tabulated for comparison (see Table VIII).

During initial operation of the HRT, its chemical processing plant has collected corrosion products at average rates of 0.32 to 1.83 g/hr (see Table IX) (3). This equals 1 to 6 ppm of solids removed per pass at the processing rate of 300 liter/hr. This is from 10 to 25 per cent of the corrosion products formed based on the corrosion rates indicated by nickel formation. The circulating solids concentrations have been below the limits of analytical detection.

Table VII. Summary of Typical Results with Preformed Oxides

Experimental Condition or Result	Units	Values or Conditions for Experiment Tests:						
Experimental Facility	--	HRT Mock-up	HRT-CPP	Loop A	Loop A	Loop A	Loop B ₂	Glass Loop
Run No.	--	--	--	LR-50	LR-S-15 to LR-S-24	LR-S-34- LR-S-38	LB ₂ -S-4	GL-6 through GL-11
Material Used	--	Mixed Oxides	Mixed Oxides	ZrO ₂	ZrO ₂	ZrO ₂	ZrO ₂	ZrO ₂
Temperatures	°C	280	295	300	115-260	70	140	47-77
Amount of Solids Added	Grams	1042	1468	15.4	0.5 to 1.5	.38-1.3	22	0.4
Amounts Recovered:								
Underflow Receiver	%	23	53	87	--	--	23	--
Samples	%	1	--	3	--	4-25	23	--
End of Run Drain	%	1	17	10	--	15-150	24	45-80
Other	%	35	13	--	--	20-55	7	20-55
Total Recovery	%	60	83	100	--	70-190	77	85-110
Amounts of Solids Circulating after 4 hr	%	5 to 50	1 to 10	60	25-50	2-15	50	70-90

Table VIII. Properties of Simulated Insoluble Corrosion Products

Properties	Units	Values obtained for:							
		ZrO ₂			Iron Oxides	ThO ₂	Mixed Corrosion Product Oxides		
Method of Preparation	--	Hydrolysis in Loop	Preformed	Preformed	Hydrolysis in Loop	Oxalate Decomposition	Preformed	Preformed	Preformed
Where Used	--	Loop A	Loop A	Loop B-2	Loop B	Loop B-2	HRT Mock-Up	HRT-CPP	Laboratory Studies
Purpose of Studies	--	Behavior of Solids	Behavior of Solids	Behavior of Solids	Hydroclone Efficiency	Hydroclone Efficiency	Behavior of Solids	Behavior of Solids	High Temperature Settling rates
Compositions:									
ZrO ₂	Wt %	> 90	100	100	--	--	47	47	46
Fe ₂ O ₃	Wt %	--	--	--	> 90	--	40	40	41
Cr ₂ O ₃	Wt %	--	--	--	--	--	13	13	13
(RE) ₂ (SO ₄) ₃	Wt %	--	--	--	--	--	0	0	0
ThO ₂	Wt %	--	--	--	--	100	0	0	0
Size Distributions:									
40% Smaller Than	Microns	0.7	--	--	0.2	0.9	0.5	--	0.3
Mean Size	Microns	1.0	--	< 0.1	0.3	1.1	0.7	0.7	1.
80% Smaller Than	Microns	4.0	0.2	0.2	0.6	1.5	2.3	2.5	5.

Table IX. Collection of Corrosion Products by
the HRT-Chemical Processing Plant

Quantity	Units	Results for Chemical Plant Run Number					
		16-1	16-2	16-3	17-4	17-5	17-6
Operating Time	hours	120	310	339	290	439	101
Corrosion products Collected	g	150	99	115	530	145	51
Average Rate	g/hr	1.25	0.32	0.34	1.83	0.33	0.50
Compositions:							
Fe	%	52	48	56	22	19	19
Cr	%	5	5	5	4	4	4
Ni	%	--	3	0	0	0.3	0
Zr	%	11	8	6	45	49	48
Ti	%	0	0	0	0.2	1	0.8
Ag	%	0	0	0	0	0.1	0.2

The collection rate, the collection efficiency, and the concentration in circulation are all in the low end of the ranges predicted from non-radiative studies of corrosion product behavior. These values appear to be increasing as operating time is accumulated and the asymptotic values may be within the 25 to 60% collection efficiency and 10 to 100 ppm circulating solids concentrations originally expected.

Changes in the composition of the collected corrosion products (see Table IX) would be expected from the observed corrosion changes. The appearance of titanium in Run No. 17-4 followed the installation of a titanium corrosion specimen holder which was later found to be attacked. The increased zirconium content agrees with the observed core vessel corrosion. The amount of zirconium collected was equivalent to about 0.001 in. over the entire core vessel inside surface. Ultrasonic measurements indicated thickness decreases of up to 0.050 inches.

Measurements of Fe-59 activity in the corrosion products deposited on sample coupons indicated that they had circulated about one-half hour before being deposited. This 30 minute circulation time agrees with several other estimations made for the HRT system. For the thirty minute circulation time, the chemical processing plant collection efficiency would be about 10 per cent for a 40 per cent hydroclone efficiency and 25 per cent for a 100 per cent hydroclone efficiency.

5.0 CONCLUSIONS

In an aqueous UO_2SO_4 solution used as a nuclear reactor fuel at over 200°C , the insoluble fission products will quickly deposit on surfaces exposed to the solution. The solubilities for rare earth sulfates decrease as the temperature increases. These salts will show a strong preference for deposition on the hottest surfaces exposed to solution and will tend to redissolve as the temperatures are lowered. The concentrations in circulating streams approach equilibrium values which appear to be the solubilities at the temperature of the hottest surface in the system. The fission products which hydrolyze to oxides or which are insoluble at all temperatures will remain where deposited either on circulating corrosion products or on the container walls. For initial operation of a reactor system, the concentration of circulating solids was low and very low percentages ($\sim 1\%$) of the insoluble fission products were collected by a solid-liquid separator on a by-pass stream.

The corrosion product oxides released into the circulating fuel solution as solids circulate for short periods of time. The geometries, including the types of surface, the surface to volume ratios, the wall to fluid temperature differences, and the existence of dead end or no flow regions, is a controlling factor when comparing different systems.

Quantitative predictions for the operation of the HRT Chemical Processing Plant were uncertain due to uncertainties concerning the characteristics of reactor solids and the effects of the complex reactor system geometry (8). Results for insoluble fission products agree well with the behavior of $\text{Zr}(\text{SO}_4)_2$, $\text{Nd}_2(\text{SO}_4)_3$, and mixed rare earth sulfates in development loops. The observed collection of 10 to 25 per cent of the Homogeneous Reactor Test corrosion products by its Chemical Processing Plant during initial periods of operation is in agreement with the observed behavior of preformed corrosion products.

The problems of obtaining representative samples and accurate analyses for the conditions studied (up to 320°C, 2000 psi and down to 1 ppm concentrations) limited the results obtained. Circulation through bombs was the only satisfactory method of obtaining samples or of adding insoluble material to loops at high temperatures and pressures. Radioactive tracers gave the most accurate analyses of the low concentrations of rare earths and zirconium.

6.0 REFERENCES

- (1) Ferguson, D. E., R. E. Leuze, R. A. McNees, "Predicted Behavior of Fission Products in the HRT", ORNL-CF-56-2-87 (Feb. 16, 1956)
- (2) Briggs, R. B., et al, "Homogeneous Reactor Project Quarterly Progress Report for Period Ending April 30, 1957", ORNL-2331, (Aug. 14, 1957)
- (3) Briggs, R. B., et al, "Homogeneous Reactor Project Quarterly Progress Report for Period Ending October 31, 1958", ORNL-2654, (, 1959)
- (4) Horton, R. W., J. R. Bowen, P. A. Haas, "Loop Studies on the Behavior of Preformed ZrO_2 in Uranyl Sulfate Solution", ORNL-2577 (Oct. 22, 1958)
- (5) Culler, F. L., et al, "Chemical Technology Division Monthly Progress Report for July 1957", ORNL-2385 (Nov. 14, 1957)
- (6) Culler, F. L., et al, "Chemical Technology Division Monthly Progress Report for September, 1957", ORNL-2416 (Dec. 23, 1957)
- (7) Briggs, R. B., et al, "Homogeneous Reactor Project Quarterly Progress Report for Period Ending January 31, 1957", ORNL-2272 (Apr. 3, 1957)
- (8) Haas, P. A., et al, "HRP-CP Conclusions Concerning the Predicted Behavior of Insoluble Corrosion and Fission Products in the HRT", ORNL-CF-58-1-97 (Jan. 23, 1958)

DISTRIBUTION

1. S. E. Beall
2. R. E. Blanco
3. E. G. Bohlmann
4. J. C. Bresee
5. K. B. Brown
6. F. R. Bruce
7. W. D. Burch
8. F. L. Culler, Jr.
9. W. K. Eister
10. D. E. Ferguson
11. H. E. Goeller
12. A. T. Gresky
- 13-32. P. A. Haas
33. E. Lamb
34. R. B. Lindauer
35. R. N. Lyon
36. R. A. McNees
37. M. J. Skinner
38. E. H. Taylor
39. W. E. Unger
40. H. O. Weeren
41. C. E. Winters
42. HRP Director's Office
- 43-44. Laboratory Records
45. Laboratory Records (RC)
- 46-47. Central Research Library
48. E. J. Murphy
- 49-63. TISE, AEC, Oak Ridge
64. Document Reference Section