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Gentlemen:

Subject: Transmittal of Semi-Annual Report, Coolant Technology
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As required by TMC Procedures defined in the reference document, the
semi-annual report on Coolant Technology, RI 1.9, for the period
November, 1980, through April, 1981, is transmitted herewith. The
contribution is on camera-ready copy and follows the format explained
in the reference document.

Permission for final release of the paper has not yet been received,
but has been requested through the Rockwell International/ESG Patent
Office.

Very truly yours,

M. S. Werkema
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SUMMARY OF ROCKWELL INTERNATIONAL -
ENERGY SYSTEMS GROUP CONTRIBUTION

In the decontamination task, emphasis during this report period was on determining the effect of various sensitization conditions on the metal removal rate for various stainless steel alloys, using the reference decontamination process. An accurate prediction of metal removal rate is necessary to determine the optimum process time.

Results to date indicate that alloys exposed to sodium at reactor conditions show a higher metal removal rate than the same types of alloys exposed to equivalent time-temperature conditions in a vacuum.

Other decontamination work included preparations for determining the effect of the reference decontamination process on hardfacing alloys and assistance in design modifications of the Clinch River Reactor decontamination system.

In the program task to develop an evaporative process to remove sodium from a full-size fuel subassembly, progress was made in the final assembly of the evaporation system. The test article, a fuel subassembly, was modified by adding heaters to simulate gamma heating. Thermocouples were attached at suitable internal and external positions. The vacuum containment system was assembled and leak checked. The assembly of the system is progressing on schedule and will be completed during the next report period.

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ROCKWELL INTERNATIONAL - ENERGY SYSTEMS GROUP

E. F. Hill

3.1 Decontamination

3.1.1 Introduction

The justification for the Liquid Metal Fast Breeder Reactor (LMFBR) Decontamination Program is to minimize radiation exposure during contact maintenance of sodium-exposed components. Present projections show that without a major breakthrough in radionuclide transport control, LMFBR components will become too radioactive for contact maintenance early in their life.^{1,2} The alternative is to develop decontamination methods which will remove much of the deeply diffused radionuclides without damaging the components beyond limits of acceptability.

The Department of Energy (DOE) decontamination program has been underway since 1975 and prior results are discussed in references³ to ¹⁵.

As a result of prior work, a chemical decontamination process was developed, based on a mixture of glycolic (hydroxyacetic) and citric acids, called the GCA process.¹⁴ The metal removal tests described in this report were obtained using the GCA process and the results may be used to revise the process specification.

The laboratory investigation undertaken during this report period addresses the development of a method of estimating how long a reactor component will need to be treated by the GCA process to achieve the desired degree of decontamination. Problems arise when several alloys are used to manufacture a component. Since metal must be removed from sodium-exposed LMFBR components in order to reach and dissolve deeply diffused radioisotopes, it is necessary to be able to predict the rate of metal removal to know when to stop the process. The rate of metal removal is related to the prior time/temperature history of a given component and the chemistry of its alloys and of the exposure medium. The tests determined, in a quantitative way, some of the variables

affecting metal removal rates for stainless steel alloys when they are treated by the GCA process. Special attention is being given to the problems which arise when both AISI 304 and 316 stainless steel alloys are used in the same component.

3.1.2 Scope of Investigations

The work completed during this period had four objectives:

1. determine the metal removal rates obtained with the GCA process for stainless steel alloys sensitized 15 000 and 20 000 hours at 811K (1000°F) in vacuum (traveler specimens) and compare the results obtained during this period with prior results;
2. prepare sensitized test specimens of hardfacing alloys;
3. assist in the design of the decontamination process equipment for the Clinch River Breeder Reactor Plant (CRBRP);
4. prepare papers for the U. S A./Japanese Specialists' Meeting, July 13-14, 1981.

3.1.3 Experimental Results

3.1.3.1 Metal Removal Results with Traveler Specimens

The traveler investigation is part of an effort to develop prediction techniques for achieving a desired degree of decontamination of LMFBR components. The rate of metal removal for various alloys is the key parameter for process control.

The rate of metal removal obtained using the GCA process varies with alloy type, sensitization conditions, exposure medium and dissolved oxygen concentration in the process solution. The GCA Process Specification¹⁴ requires that traveler specimens shall be prepared from archive samples of the metal heats used in a component and that the traveler shall be exposed to the same conditions as the component. Specimens

are then to be used in laboratory metal removal tests to determine the appropriate decontamination process time. However, it has not been possible to reach agreement with reactor designers that test specimens may be placed in an operating reactor. Alternatively, specimens may be exposed in a vacuum chamber or a sodium loop to conditions which simulate those in the reactor.

The traveler specimens tested during this period were exposed in a vacuum chamber. They are described in Ref.¹⁸. Briefly, various well-characterized heats of AISI 304 wrought stainless steel (SS), AISI 316 wrought SS and CF8M (commonly called 316 cast SS) were sensitized in a vacuum furnace ($1\text{E}-04$ Pa) at 811K (1000°F) for $5.4\text{ E}+07\text{s}$ and $7.2\text{ E}+07\text{s}$ (15 000 and 20 000 hours). These conditions are typical of hot leg conditions two to three years in a reactor.

Metal removal tests were then run using these specimens with the GCA process¹⁰ with excellent dissolved oxygen control, varying from 0.5 to 3.5 parts per billion (ppb) by weight. The results for 316 SS alloys for this series of tests are shown in Figure 3.1. Some prior results on these alloys sensitized at 977K for $1.44\text{ E}+04\text{s}$ (1300°F for four hours) are also shown. Qualitatively, the effect of oxygen on metal removal is similar to that previously shown for 304 SS alloys¹⁸. These data show that the short time sensitization at a higher temperature (977K) produces the same degree of sensitization as in the long time tests at lower temperatures (811K). This is consistent with the sensitization susceptibility for 304 SS (Figure 2, Ref.⁵).

The metal removal rate obtained in prior work for sodium-sensitized specimens¹⁸ is roughly three times higher than for vacuum sensitized of the same heats. Figure 3.2 shows metal removal rates¹⁸ for sodium-sensitized specimens compared to the rates for vacuum sensitized specimens (Figure 3.1). The specimens were from the same heats for the two tests. Since the sodium exposure time at reactor conditions ($3\text{ E}+07\text{s}$) is less than the long time vacuum exposure, the differences for actual components may be even greater than that shown in Figure 3.2.

The consequence of these findings is that traveler specimens should be sensitized in a sodium loop operating at the same conditions as the

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Fig. 3.1, Effect of oxygen on the metal removal rate of vacuum sensitized wrought and cast stainless steel (GCA process, 90°C)

Rockwell Dwg. 81-MA6-35-14

Fig. 3.2. Removal ratio - sodium exposed stainless steel compared to vacuum exposed specimens 811K, 3E + .075 or more (GCA process, 90°C)

reactor. However, further work may show that it is possible to vacuum sensitize for short times and use a multiplication factor to estimate the corrosion rate for the various alloys and heats used in the reactor component.

A large difference in metal removal rates between 304 and 316 stainless steel alloys has been previously reported for sodium exposure¹⁸. Differences between the alloys appear to be even greater for the long-time sensitized specimens used in the current investigation. One heat of 304 SS (Heat No. 74966) shows almost 50% weight loss in 14 days at 90°C in the GCA solution while for both wrought and cast 316 alloys, metal removal is less than 4%. The other 304 heats tested were not attacked to nearly the same degree but all of the observed rates for type 304 are high enough to be of concern for a reactor component intended for reuse. The conditions used in the test were those required for 316 SS¹⁴ and are the conditions required if any part of the component is made of that alloy.

Data on the various alloys tested are shown in Table 3.1. The highest and lowest rate of metal removal differ by a factor of almost 100. Since the test specimens likely do not represent the extremes of heats in actual components, the potential problem in deciding when to stop the decontamination process, when mixed alloy is present in a component, is obvious.

This information should be taken into consideration when designing hot leg components, since using only wrought and cast 316 alloys would greatly simplify decontamination for reuse. In addition, the potential for grain boundary attack is greatly minimized when 316 alloys are used, so inspection for requalification should be simplified.

3.1.3.2 Hardfacing Corrosion Rate Studies

Colmonoy[®] 5 and 6 will be used as hardfacing alloys for bearing surfaces in CRBRP. These are high nickel alloys with chromium and boron additives. The objective of this study is to determine the corrosion

behavior of these alloys during decontamination by the GCA process.

The test specimens were prepared last fiscal year by the same process and vendor selected for the CRBRP pumps. The backing alloy is a certified heat of AISI 316 SS.

The first step in testing these specimens was to vacuum sensitize them by the standard short time procedure. All specimens were sensitized during the report period and stored in an argon atmosphere.

Table 3.1 Typical metal removal rates for stainless steel alloys (GCA process, 90°C, 0.5-3.5 ppb oxygen, 14 days, sensitized 811K, (1000 F) 7.2 E+07s (20 000 hr)

Heat no.	Alloy type	Wt. loss kg	Metal Removal Rate	
			m/s	(mil/day)
74966	304 Wrought	3.3 E-03	1.9 E-04	(0.65)
55183	304 Wrought	4.3 E-04	1.6 E-05	(0.056)
8631438	304 Wrought	2.1 E-04	1.3 E-05	(0.043)
CF8M70	316 Cast	1.4 E-04	8.5 E-06	(0.029)
CF8M73	316 Cast	2.0 E-05	1.1 E-05	(0.037)
27332-03	316 Wrought	4.2 E-05	2.3 E-06	(0.008)
47582	316 Wrought	4.9 E-05	2.8 E-06	(0.0095)

A procedure for separately determining the corrosion rate of the hardfacing material, the 316 SS support and the interface was developed and proved during this period. A masking tape of TFE[®] (teflon) has been found suitable for use in the hot GCA acids. The tape is treated with sodium so that a silicone adhesive can be applied. In the first step, only the hardfacing is exposed, next only the stainless steel is exposed and then the entire piece is exposed, including the interface. Two tests have been completed. In each test, there were six specimens with hardfacing exposed. A 316 control specimen without hardfacing or masking was included in each batch.

The first results show that the corrosion rates of Colomony[®] 5 and 6 are comparable, but both appear to have a higher corrosion rate than the 316 SS heat used as a backing material. In two two-week tests at 90°C in the GCA solution at a dissolved oxygen concentration of about 2 ppb in each, the metal removed from the hardfacing specimens varied from 3 μm (0.12 mil) to 13 μm (0.5 mil). It is not yet clear whether this variability is caused by a need to refine the experimental techniques used or whether it reflects the variability in the process of applying the hardfacing materials. The control specimens of the original stainless steel used as the substrate material for the hardfacing alloys showed excellent reproducibility in the two tests, 3 μm (0.12 mil) and 3.3 μm (0.13 mil).

3.1.4 Assistance to CRBRP Decontamination System (44) Design

The CRBRP decontamination system was designed before the GCA process was developed. Consequently, several changes and additions need to be made to the equipment. In addition, the sodium removal and decontamination processes were developed separately and some interface problems need to be resolved. Most of the latter problems have been handled by joint action between Hanford Engineering Development Laboratories (HEDL) and Energy Systems Group (ESG).

The major equipment problems at CRBRP were the lack of a separate mixing tank, no sparger design and inadequate instrumentation. The solutions to these problems were (1) a suitable tank was found in System 24; (2) the Pall Corporation sintered 316 SS spargers were tested and found to have an acceptable corrosion rate equivalent to 2.5 μm (0.1 mil) per test; (3) suitable oxygen control instrumentation has been described and specified for both the nitrogen and the acid solution.

Any alkali clinging to the component after sodium removal will neutralize some of the GCA acid. However, calculations show that this amount is within allowable range of the acid concentrations. Thus, the final rinse after sodium removal can be eliminated with a resulting

savings in time, water consumption and waste water evaporation cost.

3.1.5 Preparation of Papers for Japanese/U.S. Specialists' Meeting on Sodium Removal and Decontamination

At the subject meeting in Richland, Washington, July 13-14, two papers describing decontamination studies will be presented. One paper is a description of the GCA process with emphasis on the novel features of the acids used, oxygen control and the metal removal behavior of various alloys of stainless steel. The other paper describes the initial discovery during this program that the diffusion of 54 Mn in 304 SS was much greater than for 316 SS.

3.1.6 Summary and Conclusions

The investigative work done during this period includes studies (1) to develop a means of predicting the optimum process time for GCA decontamination, (2) to develop procedures for determining the corrosion rate of hardfacing alloys, (3) to assist in the design of the decontamination system for the CRBRP, and (4) to prepare papers for the Japanese/U.S. Specialists' Meeting in July.

It was concluded that a sodium loop may be needed to properly sensitize test specimens for use in preliminary tests to determine the optimum decontamination process time. However, further studies may show that process time predictions can be made with sufficient accuracy using a relatively simple short time vacuum sensitization treatment. This question is expected to be resolved during the next report period. The complications arising from using both 304 and 316 SS alloys in the same component are discussed in this report.

Procedures have been developed and testing has been initiated to determine the effect of the GCA decontamination process on the hardfacing alloys, Colmonoy[®] 5 and 6, in CRBRP pumps. Complete results of

these tests will be available in the next report period.

Assistance has been provided to CRBRP in the design, operation and instrumentation of the decontamination system for reactor components. Most of the remaining problems with this system have now been resolved.

Two papers on decontamination for the Japanese/U.S. Specialists' Meeting were prepared.

3.2 Sodium Evaporation from a Full-Size Fuel Subassembly Test Article

3.2.1 Introduction

Reactor components from sodium-cooled systems must have the sodium removed before they can be further processed. The present objective is to develop a method of removing sodium from spent fuel subassemblies so they can be stored in a water pit until they can be reprocessed. An important potential advantage of the evaporation process over other processes is that it may remove sodium from the interior of failed fuel pins. (19, 20, 21)

For the current experimental program, an evaporation system which contains a full scale fuel subassembly as the test article is in the final stages of assembly. This system will be used in a cyclic process, alternating a vacuum step with an argon flow step. The parameters of time-temperature-pressure most suitable for removing sodium from a fuel assembly with no failed pins will be determined. If successful, the system will be used for future evaluations of the removal of sodium from a subassembly with simulated failed pins. In the test article, the heat effect of fuel is simulated by heating rods. Radioactive material is not used.

3.2.2 Scope of Investigation

The objective of the work during this period was to initiate the assembly of the evaporation system components. The system was designed and components were fabricated in prior work on this program. In this report period, the test article, a full scale simulated fuel subassembly, was modified, assembled and instrumented. Parts of the vacuum subsystem were operated to determine where modifications were needed.

A paper on the Sodium Evaporation System was prepared for the Japan/U.S. Sodium Removal and Decontamination Specialists' Meeting, July 13-14, 1981.

3.2.3 Results

The major accomplishment during this period was the partial assembly and instrumentation of the vacuum/argon sodium evaporation system. The system is illustrated in Figure 3.3 with the main subsystems and instrumentation identified. The most significant design parameters are given in Table 3.2.

Design of the sodium condenser required development of the critical parameters involved in achieving complete condensation without causing sodium entrainment in the inert gas flowing through the system. Very little information is available on this subject.

Fig. 3.3. Sodium evaporation system for fuel subassembly

Table 3.2 Design parameters of full size fuel subassembly sodium evaporation system (argon/vacuum cycle).

Argon heater rating	36 000 W
Inlet argon temperature	700 K (800°F)
Argon flow rate	0.151 kg/s (1200 lb/hr)
Exit temperature argon	366K (200°F)
First argon cycle time	3600s
First vacuum cycle time	900s
Subsequent cycle time	900s
Heater rating -gamma heat simulation	12 000 W
Sodium to be removed per run (estimated)	0.7 kg
Mechanical vacuum pumps (2) rating each	1.42 E-01 m ³ /s
Turbomolecular pump	1.4 m ³ /s
Sodium condenser surface area (liquid nitrogen cooled)	1.1 m ²
Sodium wetting temperature	811K (1000°F)

By cooling the condenser with liquid nitrogen, which also greatly reduces the argon velocity, it should be possible to prevent sodium entrainment during the argon flow part of the process cycle. No difficulty is expected in condensing sodium during the vacuum cycle.

During the design review, November, 1979, the suitability of Conflat[®] type vacuum flanges for sodium service was questioned. Although small flanges of this type have been used at EBR-II and elsewhere in sodium loops, no instance of the use of 13.25 inch (336.6 mm) O.D. flanges to contain sodium at 1000°F (538°C) is known. An analysis of this problem showed that the flanges are satisfactory for experimental use.

3.2.4 Summary and Conclusions

A system for the evaporative removal of sodium from a full-size fuel subassembly, using alternate argon-vacuum cycles, has been designed, fabricated and partially assembled.

The design parameters and process conditions which were selected for evaluation are described in this report.

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