UCRL- 84679
PREPRINT

CONF-802987-3

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OF CRUSHED AND CORED SYNROC

David G. Coles
Fernando Bazan

MASTER

Journal of Nuclear Technology
Workshop on Comparative Leaching - Behavior
of Radioactive Waste Forms - Argonne National
Laboratory - September 3 - 4, 1980

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Continuous-Flow Leaching Studies of Crushed and Cored SYNROC

David G. Coles and Fernando Bazan

ABSTRACT

Both crushed (150-300 μm) and cored (1.8 mm diameter) samples of SYNROC have been leached with the single-pass continuous-flow leaching equipment. Crushed samples of Cs-hollandite were also leached in a similar experiment. Temperatures used were 25°C and 75°C and leachates were 0.03 N NaHCO_3 and distilled water. Leaching rates from SYNROC C were ranked $\text{Cs} > \text{Sr} \geq \text{Ca} > \text{Ba} > \text{Zr}$. A comparison of leaching rates is made between crushed SYNROC, cored SYNROC, and PNL 76-68 glass beads. Problems encountered when comparing the leaching rates of different waste forms are discussed.

"Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under contract number W-7405-ENG-48."

INTRODUCTION

Immobilization of nuclear waste by incorporation into a stable waste form is a required first step in waste disposal. The rate at which the waste form releases its contained radioactivity in its final repository configuration will be a primary criterion for determining the acceptability of the disposal scheme. For the purpose of this paper, it is assumed that geologic storage will be used and that release will occur as a result of groundwater leaching. An important objective of waste disposal research is to develop a solid waste form which exhibits a very low radionuclide release rate when contacted with groundwater. Research of the past few decades has mostly concentrated on glass formulations. These products generally exhibit leach rates in the range of 1 to 10^{-3} g glass/m²·day¹. The question has not yet been answered as to what constitutes an acceptably low leach rate for a nuclear waste repository. However, in the opinion of some researchers, there are several alternative waste forms in various stages of development which have the potential to exhibit markedly reduced leach rates when compared to glass^{2,3}.

The SYNROC concept was introduced and developed by A. E. Ringwood³ of Australian National University. The objective of the SYNROC process is to immobilize nuclear wastes by incorporating or "dissolving" them in the crystal lattices of the minerals of a synthetic rock. The preferred SYNROC waste form is composed of three very refractory and leach-resistant titanate minerals - zirconolite ($\text{CaZrTi}_2\text{O}_7$), perovskite (CaTiO_3) and hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$). These minerals are closely related to natural minerals known to have been stable in a wide range of geological and geochemical environments for periods longer than one billion years. It has been shown experimentally that nearly all nuclear waste elements can be incorporated in these minerals⁴.

Concentrations of at least 10 weight percent of calcined high level waste can be immobilized in this manner. The most hazardous radwaste elements are cesium, strontium and the actinides. In SYNROC, cesium and strontium are incorporated in hollandite and perovskite respectively, while the longer-lived actinides are distributed between zirconolite and perovskite.

The Lawrence Livermore National Laboratory (LLNL) has the responsibility for developing and assessing SYNROC as an alternative waste form to glass for the U.S. defense wastes in tank storage at the Savannah River Laboratory in South Carolina. In the development of the new waste form, an important criterion in assessing various formulations is leaching characteristics. In order to compete with the more highly developed glass waste form, SYNROC must show superior leaching rates under repository conditions. The single-pass continuous-flow leach test (SPCF) was developed to simulate the conditions of a flooded repository where groundwater flows from an aquifer, through the repository, and finally back into the aquifer^{5,6}. The SPCF test is being used as a primary method for the evaluation of leaching characteristics of SYNROC waste forms. Leaching studies on nuclear explosion melt glass⁷ and PNL 76-68 glass beads doped with ^{237}Np and ^{239}Pu ⁸ have also been done using the SPCF method as part of the leach testing associated with the Waste/Rock Interactions Technology Program (WRIT)⁹. High temperature static leach tests are routinely used for internal screening of SYNROC products as they are produced. Both the SPCF and static leach tests are compatible with standard tests developed by the Materials Characterization Center (MCC)¹⁰. A modification of the SPCF leach test will be used for the MCC dynamic leach test (MCC-4).

Alternate waste forms must be judged according to their comparative leaching rate with respect to glass. The PNL 76-68 borosilicate glass is

considered to be an appropriate reference glass because it contains a full contingent of mock waste radionuclides and has been subjected to more study than any other formulation. It should be pointed out that most comparative studies have failed to consider variations in product surface conditions and the manner in which those surface areas were measured. This is particularly important when comparing such diverse waste forms as glass and ceramics. Many of the PNL 76-68 glass studies have been done on 7-8 mm diameter beads which exhibit the typically smooth, vitreous glass surface. Such surfaces lend themselves to reasonable geometric surface area determinations. The synthesis requirements and the character of the waste form itself prohibits some alternate waste forms from being made in small reproducible shapes. For example, SYNROC ceramic waste forms are made on a laboratory scale by sintering or hot pressing pellets up to 10 cm in diameter. The large pellets are then either sawed, cored, or crushed and then subsequently sieved into units which are smaller and more readily leached. Crushed samples afford high analytical sensitivity but must rely on gas adsorption for surface area determinations. Surface areas for cored and sawed samples are usually determined geometrically. Ceramic waste forms have a higher intrinsic surface area than glass due to their crystalline structure and one would expect that in the case of identically sized monoliths of SYNROC and glass, the SYNROC sample would have a significantly greater surface area. This gives glass a justifiable advantage (assuming no cracking during production) when comparing the leach rates of a monolith of each waste form placed in a repository. However, for comparison of waste form leach rates, it is imperative that both must be either 1) leached in a configuration which represents their actual surface conditions which a waste monolith would have or 2) both must be identically prepared for the leach test (by sawing or coring). In the latter case, the extra surface area introduced by the saw or core must be taken into

account since this surface area is not intrinsic but introduced by the sample preparation technique. Both saw marks and crystal plucking (ceramics) or conchoidal fracturing (glass) are common effects incurred during sample preparation. In order to determine the potential release from a repository, leach rates should be expressed (after proper normalization) in terms of geometric surface area since this represents the intrinsic leach rate of an actual monolith of waste.

EXPERIMENTAL

SPCF Leaching Technology. Leaching results reported here were done exclusively with the LLNL single-pass continuous-flow leaching of waste form samples. The test itself has been described in detail elsewhere^{5,6,7,9}. In the SPCF method, the waste form of interest is placed into the path of flowing water with the rate of water flow set to approximate values expected in actual aquifers. Volume flow rates can range from the near static value of 1 ml/day to over 500 ml/day, a value far in excess of what would be expected in an aquifer near a repository. Peristaltic pumps control the flow rates and the leachant is directed from the supply carboy, through the pump, through a cell containing the waste form, and finally into a leachate collection vessel. Analysis is then performed on the leachate for the elements or radionuclides of interest. This type of dynamic leaching experiment avoids the problem of solution saturation that is encountered with the typical static tests. It also avoids the problem of sample disturbance that occurs with modified static tests where the leachant is periodically changed.

Synthesis of SYNROC Samples: Data from leach tests of two SYNROC samples are presented in this paper. A SYNROC-C formulation containing a PNL simulated radwaste composition (PW-4B-7) was prepared by spray drying a mixture of 90 weight % SYNROC additives (TiO_2 , BaO, ZrO_2 , Al_2O_3 , and NiO) with

10% PW-4B-7 simulated radwaste. The spray-dried powder was then hot pressed in graphite for 1 hour at 1200°C to 95% of theoretical density. Figure 1 gives a schematic representation of the preparation scheme. A portion of the resultant ceramic was crushed, sieved, and the 150-300 μm ($< 48, > 100$ mesh) fraction was leached with the SPCF leach test. Fifty-four cores approximately 4.2 mm long by 1.8 mm in diameter were also leached with the SPCF system. The calculated composition for the SYNROC C samples subjected to leaching (designated S05PH4A) is given in Table I.

The second sample leached was a single-phase hollandite containing 3.8 weight % Cs_2O . This experiment was conducted in order to ascertain the ability of the hollandite phase to immobilize Cs. The sample was prepared by hot pressing spray-dried and calcined powder in graphite at 1200°C for 1 hour to $> 96\%$ of theoretical density. Figure 2 gives a schematic representation of the preparation scheme. This sample was crushed and the 150-300 μm fraction was leached by means of the SPCF leach test. The calculated composition of the Cs-bearing hollandite sample (designated S03HP3A) is given in Table II.

Leaching Experiments. Figure 3 is a schematic representation of the experimental matrix for the SYNROC C leaching test. The samples were crushed and sieved and the 150-300 μm fraction was taken for the testing. Before loading samples into the cells (3 grams/cell) the material was ultrasonically cleaned in ethyl alcohol and then air dried. An aliquot of the sample was taken for B.E.T N_2 adsorption surface area analysis. The leaching test was then begun and run for 44 days. Seven separate channels were involved. Six channels contained the 150-300 μm fraction of the crushed samples and one contained the 54 core samples. Crushed samples were run with two leachants and at two temperatures. Three samples were leached with 0.03 N NaHCO_3 water and three were leached with distilled water. Replication was achieved for

SYNTHESIS OF SYNROC C (BATCH S05)

Fig. 1

TABLE I: CALCULATED COMPOSITION OF SYNROC C (S05HP4A)*

<u>COMPOUND</u>	<u>W/O</u>	<u>COMPOUND</u>	<u>W/O</u>
TiO ₂	51.54	Y ₂ O ₃	0.15
CaO	12.72	CeO ₂	0.82
ZrO ₂	10.33	La ₂ O ₃	0.37
BaO	6.15	Pr ₆ O ₁₁	0.37
Al ₂ O ₃	7.80	Nd ₂ O ₃	1.18
Ni pwd.	3.00	Pm ₂ O ₃	0.03
UO ₂	0.05	Sm ₂ O ₃	0.23
Cr ₂ O ₃	0.09	Eu ₂ O ₃	0.05
Fe ₂ O ₃	0.37	Gd ₂ O ₃	0.03
CdO	0.02	MoO ₃	1.57
NiO	0.03	RuO ₂	0.73
P ₂ O ₅	0.17	Rh ₂ O ₃	0.12
Rb ₂ O	0.09	PdO	0.36
Cs ₂ O	0.71	Ag ₂ O	0.02
SrO	0.26	TeO ₂	0.19
			100.00

* From Hoenig et al.¹¹

SYNTHESIS OF Cs-BEARING HOLLANDITE

Fig. 2

TABLE II: CALCULATED COMPOSITION OF CS-HOLLANDITE

<u>COMPOUND</u>	<u>W/O</u>
TiO ₂	63.9
Al ₂ O ₃	13.7
BaO	18.6
Cs ₂ O	<u>3.8</u>
	100.0

* From Hoenig et al.¹¹

Fig. 3

Fig. 4

the bicarbonate channel at 25°C and for the distilled water channel at 75°C. To maximize the analytical sensitivity for the lower surface area of the core sample, it was run at 75°C with distilled water. All channels were run at a volume flow rate of 30 ml/day which corresponds to a linear flow rate of 38 cm/day or 14 m/year. Samples were collected continuously for sampling intervals of 1 day, 2 days, 3 days, 7 days, 14 days, and 28 days. These samples were then acidified with dilute HNO_3 (~0.1 N) and the entire sample or an aliquot was evaporated to dryness in the presence of 300 mg of very pure powdered cellulose. The dried powder was pressed into a pellet and analyzed using an x-ray fluorescence (XRF) spectrometer. This gave results for Ca, Sr, Ba, and Cs. Results for Ca, Sr and Zr were obtained on aliquots of the original liquids using inductively coupled plasma-optical emission spectrographic analysis (ICP-OES).

Figure 4 is a schematic representation of the experimental matrix for the Cs-bearing hollandite leaching test. It was identical to the SYNROC C test except that blank channels (no sample in cell) were added for the 0.03 N NaHCO_3 leachant at 25°C and the distilled water leachant at 75°C. No significant levels of any element were observed in either blank. Also, only crushed samples were leached in this experiment. Analysis was done by XRF. This product contained Ba, Al, Ti, and Cs oxides but only Ba and Cs were observed in the leachates.

Surface Area Measurements. We have utilized crushed samples only to increase the surface area available for leaching. On non-radioactive samples, this was necessary in order to increase analytical sensitivity. Surface area measurements on the 150-300 μm fractions for SYNROC C (S05HP4A) and Cs-Hollandite (S03HP3A) were done with both N_2 and Kr adsorption (B.E.T.). The surface area on the SYNROC C cores was done with Kr adsorption as well as

geometric measurement using a hand caliper. Results of these measurements is shown in Table III. Comparison between the N_2 and Kr method for the crushed samples indicates that the N_2 method resulted in a higher value by about a factor of two for both samples measured. N_2 is the gas commonly used for B.E.T. surface area measurements, but Kr gives a 10-fold increase in sensitivity. Therefore, Kr gas was used to measure the surface area of the 54 cores by the B.E.T. method. This was of interest in order to compare gas adsorption and geometric surface area measurements on monolithic pieces of SYNROC. The ratio of surface areas as measured by the gas method to that measured by the geometric method was 27 (Table III).

The interest in various surface area measurement methods was precipitated by the need to know whether scaling factors for gas adsorption to geometric measurements could be determined. Leach rates based on geometric surface areas are required in order to determine the expression of radionuclide release rates for large monoliths of actual waste. Leach rates determined in this manner account for the intrinsic surface features of a waste form produced by the appropriate large-scale production technology schemes. It should be reemphasized that the principal problem in using geometric surface areas occurs when comparing different waste forms whose surfaces were prepared for leaching with different techniques. A valid comparison of geometric surface areas can be done only when the waste forms were prepared (core, sawed, etc.) with identical techniques.

RESULTS AND DISCUSSION

Leaching of Crushed SYNROC C (S05HP4A). A schematic of the design of the SYNROC leaching experiment is shown in Figure 3. The leaching rate data as a function of time for this experiment is presented in Figure 5. Data are plotted for the 0.03 $NaHCO_3$ and distilled water leachants at both the 25°C

TABLE III: SURFACE AREA ANALYSIS FOR SYNROC-C AND Cs-HOLLANDITE

Sample	m^2/gm				
	BET Gas Adsorption			Hand Caliper (Geometric)	$\frac{Kr}{Geo.}$
	N_2	Kr	$\frac{N_2}{Kr}$		
Cs-Hollandite ¹ (150-300 μm)	0.080	0.052	1.5	--	--
SYNROC C ² (150-300 μm)	0.246	0.101	2.4	--	--
SYNROC C ³ (cores)	--	0.017	--	0.000625	27

1. S03HP3A

2. S05HP4A

3. 4.2 mm l x 1.8 mm d

and 75°C temperatures. The only elements observed from this nonradioactive sample were Cs, Ca, Sr, Ba, and Zr. All others (see Table I) were below the analytical detection limit for the analysis scheme. Calcium data, which mimics the behavior of Sr since both are divalent ions, was not plotted for the sake of legibility. Leach rates, expressed as grams SYNROC leached/ $m^2 \cdot day$, are based on the level of observed elements in the leachate and their respective concentration in the waste form. Error bars have been placed on only a few sets of data in order to show the quality of the data without distracting from the legibility. The error bar range is uniform for all data. The surface area analysis was done with N_2 adsorption. The gas adsorption technique constitutes a valid measure of surface area for these samples since the product was close to theoretical density.

The effect of temperature on Cs leach rate appears to have been more significant than the leachant effect (Figure 5). The 75°C leach data for Cs with both leachants was about an order of magnitude higher than the 25°C data. The effect of leachant composition on leach rate was minor and inconsistent.

In the case of Sr and Ca, there was also only a minor leachant effect on leach rate but the effect was consistent with temperature, the distilled water showing the higher leach rate at both 25°C and 75°C. The 75°C temperature showed about a factor of 3-5 higher leach rate for both leachants.

The leach rates for Ba show no leachant effects and only a small temperature effect. The leach rate in the 75°C channels was a factor of two higher than that in the 25°C channels.

Only two samples were observed to contain Zr since its level in the leachates was very near the detection limit for both analytical methods. These data are shown in Figure 5 and they are for the 75°C distilled water channels.

The leaching rates for the five elements observed are ranked as follows: $Cs > Sr \geq Ba > Zr$. Phase equilibria studies of SYNROC C⁴ have shown that Cs and Ba preferentially enter the hollandite phase and Ca and Sr enter the perovskite phase and, to a lesser extent, the zirconolite phase. Therefore hollandite is the source of Cs and Ba observed in the leachates and perovskite is the likely source for the Sr and Ca. There are three observations which suggest that the principal cations in the leachate are derived from perovskite. First, the leach rates for both Ca and Sr are nearly identical although this may be coincidental due to the fact that there are two sources for Ca in the sample. Second, perovskite has been observed to undergo incongruent dissolution in nature, i.e., rutile (TiO_2) pseudomorphs of perovskite ($CaTiO_3$) have been reported¹² indicating that the Ca has been selectively removed. Third, zirconolite is the only source of Zr in SYNROC C and its leach rate has been found to be several orders of magnitude lower than that of Ca. If Ca and Zr are removed from zirconolite at the same rate then the principal source of Ca must be a phase other than zirconolite; perovskite.

Leaching of Crushed Cs-Hollandite (S03HP3A). The schematic design for the Cs-hollandite leaching experiment is shown in Figure 4. The leaching rate of Cs-hollandite as a function of time is shown in Figure 6. The data shown is the mean of the 25°C and 75°C data. No temperature effect was observed beyond the day 2 sampling interval, therefore the data for both temperatures have been combined. There is no leachant effect for Ba. The slight leachant effect for Cs is discernable but minor when the error bars are taken into consideration. The leaching behavior for Cs and Ba from Cs-hollandite differs from the behavior in SYNROC C in that there is no temperature dependence of leach rate in the single phase sample. The leach rate for Cs at 25°C from SYNROC C is the same as the 75°C and 25°C leach rates for the

Fig. 6

Cs-hollandite. The leach rate for Ba in SYNROC C is nearly the same as it is for Cs-hollandite except that the former shows a slight temperature dependence.

A possible explanation for the noticeable temperature effect for Cs leaching in SYNROC C versus no temperature effect in the hollandite phase may be that incomplete loading of Cs has occurred in the single-phase hollandite phase. A small percentage of the total Cs may reside in a minor phase or in grain boundaries and thereby have a lower activation energy for leaching. The Cs loading in hollandite was similar in the two samples. The Cs-hollandite phase contained 3.8 wt percent Cs_2O . There was only 0.71 wt % Cs in the SYNROC C formulation but assuming that a third of the SYNROC C was hollandite and that all of Cs was incorporated into that phase, then the Cs loading factor in SYNROC C hollandite would be 2.1 weight percent. The loading factors are, therefore, at a similar level. The supposition that some Cs in Cs-hollandite may exist in interstitial spaces is currently being tested. Hot pressed Cs-hollandite will be crushed to a fine powder, washed in distilled water, dried and then hot pressed a second time. Presumably any grain boundary material will have been washed out subsequent to crushing and will not be present in the repressed sample. In turn, a temperature effect may be seen upon leaching. If it is found that all the Cs does, in fact, enter the hollandite during the initial hot pressing run, then the different leach behavior of Cs in SYNROC C and single phase material can only be due to an as yet unexplained synergistic effect between the Cs in hollandite and the other phases.

Leaching of SYNROC C Cores. The rationale for leaching discrete monoliths of SYNROC has been discussed. In order to assess the leach rate of large scale monoliths of SYNROC, glass, or other alternative waste forms, the

leach rate must be directly related to the nature of the surface area which a monolith of waste would actually have. Our goal is to be able to normalize our data as obtained from the analytically-sensitive crushed form to a monolith whose surface area is based on a geometric measurement. In order to determine the normalization factor, we have 1) leached powders and cores and investigated the difference between various surface area measurement methods and 2) have determined the leach rates of different waste forms whose surface areas have been measured with identical methods.

As mentioned earlier, nitrogen was used to measure the surface areas on the 150-300 μm size fractions for both SYNROC C and Cs-hollandite. The leach rate data in Figures 5 and 6 were calculated on the basis of this method. Both samples were also measured using the BET Kr method. Table III compares the difference in surface area as determined by BET N_2 adsorption, BET Kr adsorption, and geometric surface areas of cores. The N_2 method gave higher values by a factor of 1.5 for Cs-hollandite and 2.4 for SYNROC C. The Kr was used primarily to obtain a gas sorption measurement for core samples since the sensitivity of this method is improved by a factor of 10 over the N_2 method. This is needed because the surface area for discrete monoliths is much lower than for powders. The surface area of the cores was 27 times higher as determined by the Kr method than by a geometric surface area using a hand caliper.

Figure 7 presents a comparison of leaching data of crushed and cored SYNROC C. In both cases, the leach rate is calculated based on surface area measurements done with the BET Kr adsorption method. For Sr, Ca, and Ba the agreement between the leach rates for the two types of samples is remarkably close. For Cs, the crushed sample shows a consistently higher leach rate by a factor of about five. We have no ready explanation for this anomaly. How-

Fig. 7

ever, it has been shown that leach rates for crushed glass¹³ subjected to a static test can differ by as much as two orders of magnitude from comparable leach rates on glass cylinders. These data were based on calculated geometric surface areas for crushed samples and measured geometric surface areas for whole samples. The differences in measurement techniques alone could account for the large differences but it has also been suggested that there are fundamental differences in leaching mechanisms for crushed versus whole samples. The problems associated with leaching crushed versus whole specimens should be less acute in the SPCF system as opposed to a static system because the leachant is constantly and continually being mixed and agitated in the former scheme. In the data presented herein, sample size, i.e., crushed versus core, does not appear to be a major variable during leaching.

Leach Rate Comparison of SYNROC C with PNL 76-68 Borosilicate Glass.

Figure 8 presents a comparison of leach rates for SYNROC C cores and PNL 76-68 borosilicate glass. The leach rate data for the SYNROC C cores as calculated from BET Kr adsorption surface area analysis are shown with solid lines. Data for PNL 76-68 glass based on Na and Np leach rates as calculated from the geometric surface area of 7 mm diameter hemispherical beads are shown by means of the shaded lines⁸. These glass data were chosen to cover the broadest range of leach rate, i.e., the greatest differences in element leachability. Sodium is a small, highly-soluble monovalent ion and Np is a large actinide ion which is probably tetravalent. Their leach rates are very similar, thereby indicating that congruent dissolution of the silicate matrix is the primary leach rate mechanism. All data in this figure were obtained with experiments at 75°C, with distilled water as the leachant, and at a volume flow rate of 30 ml/day through a 1 cm diameter cell.

The SYNROC C cores used in this study are shown in Figure 9 along with

Fig. 9

the core drill and remaining SYNROC sample after the coring operation. The direct comparison of the SYNROC core data to the glass bead data as based on Kr surface area analysis for the former and geometric surface area analysis for the latter is not strictly valid because the Kr measurement tends to 1) normalize the effects of the coring operation (scoring and plucking - see photomicrograph in Figure 10) and 2) measures the intrinsic surface area of the crystalline material. In Figure 8, the leach rate for SYNROC based on Cs is presented in two ways, geometric and B.E.T. analysis. Cs was chosen because it exhibits the highest observed leach rate in our study. The upper dashed curve for Cs provides a "worst-case" representation of SYNROC compared to glass since it includes the disadvantages of the geometric surface area. The actual leach rate for SYNROC is lower than the rate based on core geometry.

Some workers argue that inert gases see a different surface than an aqueous leachant. The "range" between leach rates based on geometric and experimental derived surface areas can be adjusted by conducting ethylene glycol surface area measurements. However, for a theoretically dense and relatively inert substance, the differences between these two measurements would likely be small. The data in Figure 8 provides the best comparison between these two waste forms which can be made at this time. The SYNROC sample used in the leach test represents an initial attempt at incorporating a complex radwaste in the ceramic waste form. Optimization of the product will undoubtedly result in still lower leach rates.

The only simple way to make a direct comparison between these two waste forms (or any two) is to take core drill samples of glass and SYNROC and conduct the leach test on these cored samples. With this type of experiment, the effects due to coring would essentially be normalized and the two waste

Fig. 10

forms could be compared based on their intrinsic characteristics. We are planning such an experiment in order to make the comparison in leaching rates but also to determine differences in surface area analysis for glass by means of BET (Kr gas) and geometric techniques.

CONCLUSIONS

The dynamic leaching behavior for SYNROC C and Cs-hollandite has been determined using the SPCF leach test technique. Five elements were observed in the leachate in a test of non-radioactive SYNROC C using XRF and ICP-OES techniques for analysis. The order of leach rate of SYNROC C as determined by the five elements is as follows: $Cs > Sr \geq Ca > Ba > Zr$. Temperature dependence for leaching was greatest for Cs (nearly an order magnitude difference between 25°C and 75°C). Only minor temperature effects were observed for the other elements. Leachant composition appeared to have had little or no effect on leaching behavior.

Only Cs and Ba were observed in the leachate in the SPCF test with Cs-hollandite. No significant temperature or leachant effects were observed for this single phase material.

It was observed that the range of leach rates for these samples varies over several orders of magnitude and approaches a constant leach rate only after 20 to 40 days of test duration. This indicates that more than one leach mechanism may be operating. The data support the fact that SYNROC undergoes incongruent dissolution as expected. The leach rates determined in this study are relatively insensitive to the range of temperatures and leachant compositions used. Only Cs showed a temperature effect.

A comparison of the leaching rates between crushed and cored SYNROC C was done. No difference in leach rate was observed when based on the release

of Sr, Ca, or Ba. The crushed samples showed an increase in leach rate of about a factor of 5 when based on Cs release.

A comparison was made between the leaching rates of cored SYNROC and PNL 76-68 glass. An earlier comparison was based on sparse SYNROC¹⁴ data and is not considered as being as valid as the present study. The SYNROC and glass experiments were done in an identical fashion except that the SYNROC was core drilled and the glass beads were leached with no prior surface preparation. The Cs leach rate calculations for SYNROC were done two ways. One was based on geometric surface area and the other on the BET Kr adsorption surface area. Since the leach rate of SYNROC as based on Cs gives the highest leach rate, it is considered to be a conservative or "worst case" comparison. Based on the very conservative geometric surface area, Cs showed a comparable leach rate to both Na and Kp leach rates for glass. It is concluded that the intrinsic leach rate for SYNROC would be lower than the rate based on the geometric surface area analyses. It was also concluded that the only way to obtain a direct comparison would be to conduct tests on core drilled samples for both waste forms. This would tend to normalize the effects on the preparation technique so that the comparison would be based solely on the intrinsic surfaces of each waste form.

These data are the first controlled leaching tests on SYNROC which are relevant to repository conditions. Much more work needs to be done on subsequent SYNROC samples in order to see if the leaching behavior is similar for other formulations. The leaching mechanisms will likely be difficult to ascertain for multiphase crystalline substances. The mechanisms for the leaching of single phase glass substances are still not fully understood. For SYNROC, an attempt at understanding is just beginning.

Acknowledgments:

The authors wish to thank A. Langhorst for ICP-OES analyses, C. Slettevold for surface area analyses, R. Ryerson for SEM photography, C. Althouse for assistance on the Figures, P. Beringer for typing the manuscript, and J. Tewhey for reviewing the manuscript.

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Figure Captions

Figure 1: Synthesis of SYNROC C (Batch S05)

Figure 2: Synthesis of Cs-Bearing Hollandite

Figure 3: Experimental Design for SYNROC C (S05HP4A) Leaching Experiment

Figure 4: Experimental Design for Cs-Hollandite (S03HP3A) Leaching Experiment

Figure 5: Leaching Rate vs Time for SYNROC C (S05HP4A). Crushed samples (150-300 μm) were leached and their surface areas were determined by BET N_2 adsorption.

Figure 6: Leaching Rate vs Time for Cs-Hollandite (S03HP3A). Crushed samples (150-300 μm) were leached and their surface areas were determined by BET N_2 adsorption.

Figure 7: Comparison of Leaching Rates for Cored and Crushed SYNROC C. Surface areas were determined by BET Kr adsorption for both cored and crushed samples. Cored samples were 4.2 mm long by 1.8 mm diameter. Crushed samples were sieved and the 150-300 μm fraction used for leaching.

Figure 8: Leach Rate Comparison of SYNROC C Cores and PNL 76-68 Glass Beads

Figure 9: Photograph of SYNROC C Cores (Preparation S05HP4A) with Diamond Core Drill and Cored Sample

Figure 10: Photomicrograph of the Surface of a SYNROC C Core. Note the grooves and depressions. Depressions are due to crystal plucking. White bar represents 100 μm .