JOURNAL OF MATERIALS SCIENCE 17 (1982) 849–855

$CsAlSi_5O_{12}$: a possible host for ^{137}Cs immobilization

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$CsAlSi_5O_{12}$ exhibits more acid resistance than pollucite ($CsAlSi_2O_6$). At pH values of 1.02 and 1.40, the extraction of Cs from $CsAlSi_5O_{12}$ at 25° C was approximately proportional to the square root of leach time. The Cs extraction at 25° C varied as $[H^+]^{0.36}$ over the pH range of 1 to 6. Also, the Cs extraction in various brines at 300° C and 30 MPa was comparable with that for pollucite. $CsAlSi_5O_{12}$ can be crystallized at about 1000° C from calcines if a small amount of CaO is present, but, in the absence of such sintering aids, crystallization temperatures of about 1400° C are necessary. Compatibility data were also obtained with respect to several other phases with which $CsAlSi_5O_{12}$ might be expected to co-exist in tailored ceramics designed for high-level defence waste.

1. Introduction

The immobilization of ^{137}Cs is an important problem in radioactive waste mangement. Although ^{137}Cs can be readily incorporated in waste glasses, the crystalline tailored-ceramic approach [1–5] may present a more attractive alternative. In this latter approach, pollucite, $CsAlSi_2O_6$, is a possible host for ^{137}Cs removed from radioactive waste supernates at the Rockwell Hanford Operations Site U.S.A. [6]. Pollucite also forms as the Cs host in the tailored ceramic simulations designed by McCarthy [1–3] for reprocessing wastes. Barium hollandite, nominally $BaAl_2Ti_6O_{16}$, is the Cs host in the titanate tailored ceramic simulations [4, 5].

The higher Si–Al ratio in $CsAlSi_5O_{12}$ relative to pollucite would suggest, by analogy with the well-known [7] property of zeolites, that $CsAlSi_5O_{12}$ would have more acid leach resistance than pollucite. $CsAlSi_5O_{12}$ was first reported to be synthesized from a melt [8] and was present as an unwanted phase in ceramic preparations of $CsAlSiO_4$ and $CsAlSi_2O_6$ stoichiometries [9, 10]. It also has been reported to form on heating certain Cs-loaded mordenites [11], but does not form in some others [12].

2. Experimental procedure

Ceramic materials for leach and compatibility studies were made from Al and Cs nitrate solutions which were mixed with an ammonia-stabilized SiO_2 emulsion. In order to avoid formation of undesired Cs-bearing phases such as pollucite, a stoichiometry which was 20% deficient in Cs was usually used. The dried mixtures were calcined at 600° C, cold-pressed into 12.7 mm diameter pellets under a pressure of approximately 200 MPa, and fired in air.

For the leach studies, the pellets were fired at 1400° C for 2 days. Well-crystallized $CsAlSi_5O_{12}$ was obtained. A few very weak extra X-ray diffraction peaks, presumably due to aluminosilicates, were also detected. No other Cs-bearing phase was detected. Chemical analysis of the product gave values in good agreement with those expected in the absence of Cs loss by volatilization.

Since $CsAlSi_5O_{12}$ was reported to form in heated mordenite [11] some studies of Cs-loaded zeolites were made in the present work. One of the zeolites studied was Norton "Zeolon" mordenite which has already been investigated [12]. The other zeolite was "Ion-Siv IE-95", a mixture of chabazite and erionite. This latter material is a possible material for ^{137}Cs removal from radioactive waste supernates at the Savannah River Laboratory, U.S.A.

For dissolution studies at 25° C, one-gram samples of $-60+100$ mesh powder were each

0022–2461/82/030849–07$03.34/0

placed in 100 ml of solvent. The sized powders were washed briefly in de-ionized water and acetone to remove fine particles adhering to the larger particles. The solvent consisted of deionized water which was adjusted to a given pH by the addition of a few drops of HCl or KOH. The reaction mixtures were contained in polypropylene flasks, which exhibited no measurable transpiration losses in prolonged tests, and which were placed in a temperature-controlled shaker bath. To follow the time dependence of the leach behaviour, 1 ml aliquots were periodically withdrawn, added to 10 ml of acidified water, and spectrophotometrically analysed for the cation of interest.

In high-temperature "hydrothermal" studies, 20 mg of $-230+325$ mesh powder, together with 200 μl of leachant, were sealed inside a gold capsule and the capsule was placed in an autoclave and maintained at 300° C and 30 MPa for 14 days. The leachants were de-ionized water and various chloride solutions. After treatment, the solutions were spectrophotometrically analysed and the separated solids were studied by X-ray diffraction. Surface areas of powders were measured by the BET technique using N_2 gas.

X-ray powder diffraction was carried out with a standard diffractometer using graphite-monochromated CuKα radiation.

3. Results

3.1. Dissolution behaviour

3.1.1. Experiments at 25° C

Preliminary experiments showed the Cs extraction from $CsAlSi_5O_{12}$ was very small for pH values between about 3 and 12. Accordingly, the most detailed kinetic studies were conducted at pH values of 1.02 and 1.40. Fig. 1 presents data collected over a 70-day period. Also shown are some comparative results (Adl *et al.* [13]) for natural pollucite granules having the same mesh size as the $CsAlSi_5O_{12}$. In neither case was any pH drift noted over the duration of the experiments.

Fig. 2 illustrates the dependence of the Cs extraction after 50 days on pH in the acid range. The slope of the linear log [Cs] against pH relation was found to be -0.36.

3.1.2. Experiments at 300° C and 30 MPa

The results of the high-temperature leach studies for $CsAlSi_5O_{12}$ are given in Table I. Also shown are comparative data obtained on similarly-sized synthetic (phase-pure) pollucite granules, which were prepared from a calcine sintered at 1400° C for 2 days.

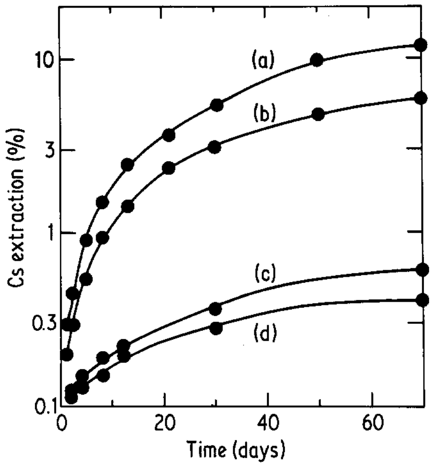

Figure 1 Time dependence of percentage Cs extraction for synthetic $CsAlSi_5O_{12}$ and natural pollucite at pH = 1.02 and 1.40, at 25° C. Curves a and b are the results for the pollucite at pH = 1.02 and 1.40, respectively, while curves c and d are the corresponding results for $CsAlSi_5O_{12}$.

3.2. Crystallization behaviour

A preparation was made which was chemically similar to that used in the study of the dissolution behaviour of $CsAlSi_5O_{12}$. However, instead of firing it directly at 1400° C it was fired at progressively higher temperatures in the 900 to 1400° C range after calcination and cold pressing. Two pellets were used and heated together. One

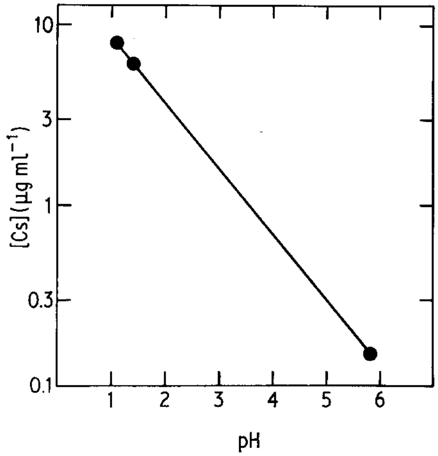

Figure 2 50-day Cs extraction for $CsAlSi_5O_{12}$ at 25° C as a function of pH in the acid range.

TABLE I 14-day Cs extraction rates* for synthetic pollucite and $CsAlSi_5O_{12}$ in various leachants at 300° C and 30 MPa

Leachant	Pollucite		$CsAlSi_5O_{12}$	
	Rate*	Extra X-ray lines (nm)	Rate*	Extra X-ray lines (nm)
Deionized H_2O	0.15	–	0.31	–
3M KCl	–	–	6.9	K-feldspar + 0.84
3M $MgCl_2$	9.2	1.13, 0.463	4.4	0.84, 0.476, 0.458, 0.391, 0.384
NBT-6 brine†	6.7	1.10, 0.47, 0.45	4.9	0.84, 0.458

*Rates are given in gm m^{-2} day^{-1}, based on BET surface areas, and are normalized with respect to the Cs contents of the starting materials. All the extra X-ray lines were relatively weak.

†NBT-6 brine is composed of 10 wt % $MgCl_2$, 10 wt % $CaCl_2$, 5 wt % KCl, 5 wt % NaCl and 70 wt % H_2O.

was studied gravimetrically and the other was studied by X-ray diffraction. The results are shown in Table II; one obvious conclusion is that a firing temperature of about 1400° C is required in order to obtain good crystallization.

In order to lower the crystallization temperature, various materials were added. A calcine of $Cs_{0.8}AlSi_5O_{12}$ stoichiometry was made up, pulverized, and divided into aliquots. Various metal oxides were added to different aliquots by mixing in appropriate quantities of nitrate solutions of Mg, Ca, Na or Pb, H_3BO_3 solution, or a slurry of TiO_2 (anatase) in water. After slurrying with additional water as necessary, drying and recalcining, pellets were made as before using a pressure of 200 MPa. In comparative tests, all pellets were fired together for 3 h.

In a test at 1200° C using 1 wt % of admixed metal oxide, good crystallization of $CsAlSi_5O_{12}$ was only achieved with the MgO additive. The other preparations were mostly amorphous with some poorly-crystallized pollucite. However, some $CsAlSi_5O_{12}$ was observed in the preparation to which the CaO was added.

In other tests 0 to 4 wt % of MgO or CaO was added and firings were conducted at 800 to 1100° C. No samples displayed observable crystallization after firing at 800° C or 900° C. After firing at 1000° C, all samples to which MgO was added and the one sample containing 1 wt % of CaO were amorphous. However, the sample containing 2 wt % of CaO contained some crystalline $CsAlSi_5O_{12}$ and the samples containing 3 and 4 wt % of CaO had fully crystallized into $CsAlSi_5O_{12}$. Samples fired at 1100° C were partly crystalline when they contained MgO and were fully crystalline if they contained 2 to 4 wt % of CaO.

Near-saturation loadings of Cs by ion-exchange in "Ion-siv IE-95" zeolite resulted in a mixture of pollucite and $CsAlSi_5O_{12}$ on firing at 1000 to 1200° C. Virtually phase-pure $CsAlSi_5O_{12}$ was formed on firing similarly-loaded mordenite at 1000 to 1200° C. This result was in agreement with the findings of Forberg and Westermark [11], but not with those of Mimura and Kanno [12]. Perhaps chemical differences among the samples were responsible for the lack of agreement. The precise temperature at which crystallization occurred in the present work varied from batch to batch and the details of the Cs loading; the critical factor appeared to be the degree of exchange of divalent cations present in the zeolites. However, further work is needed to clarify this point in detail. This latter feature followed from the observations on the effect of additives on the crystallization of calcines of $Cs_{0.8}AlSi_5O_{12}$ stoichiometry. Some chemical analyses were made and Cs losses on firing were small, probably less than 2 %.

TABLE II Gravimetric and X-ray results on sequential sintering in air of calcines of $Cs_{0.8}AlSi_5O_{12}$ stoichiometry

Heat treatment	Total weight loss (%)	X-ray results
24 h at 900° C	4.24	Amorphous
2 h at 1100° C	4.35	Amorphous + small amount of $CsAlSi_5O_{12}$
2 h at 1250° C	4.44	Amorphous + small amount of $CsAlSi_5O_{12}$
2 h at 1400° C	4.49	Mainly $CsAlSi_5O_{12}$ + small amounts of amorphous material and $CsAlSi_2O_6$
48 h at 1400° C	5.94	Mainly $CsAlSi_5O_{12}$ + some $CsAlSi_2O_6$

At low ($<20\%$ of saturation) Cs-loading, no recognizable crystalline Cs aluminosilicates were formed on high-temperature firing. These preparations melted on heating to 1200° C. These results were not unexpected in view of the results on the compatibility of nepheline and $CsAlSi_5O_{12}$–$CsAlSi_2O_6$ (see Section 3.3).

3.3. Compatibility

The compatibility of $CsAlSi_5O_{12}$ with various phases possibly occurring in tailored ceramics designed for immobilization of radioactive wastes at the Savannah River Laboratory [14–16] was studied. These phases were α-Al_2O_3, nepheline ($NaAlSiO_4$), (Fe, Ni) spinel and UO_{2+x} (uraninite).

The results were not entirely conclusive, because of the aforementioned difficulty of crystallizing $CsAlSi_5O_{12}$ from calcines. Calcines of $CsAlSi_5O_{12}$ composition were mixed in various proportions with each of the calcines corresponding to the other phases of interest. The mixtures were pelletized and fired at 1200° C for 2 h. For mixtures containing nepheline and α-Al_2O_3, firing was performed in air and for the mixtures containing spinel and uraninite the firings were carried out in sealed Pt capsules. For 3:1 and 1:1 nepheline–$CsAlSi_5O_{12}$ (by weight) mixtures, the crystalline products were pollucite and nepheline, but for a 10:1 nepheline–$CsAlSi_5O_{12}$ mixture only crystalline nepheline was observed. For the other mixtures, only the spinel, uraninite, or alumina crystallized.

Part of the $CsAlSi_5O_{12}$ calcine was then fired at 1400° C to produce a mixture of crystalline pollucite and $CsAlSi_5O_{12}$. This was mixed with the other calcines and fired as previously. There was no evidence of reaction of the spinel, uraninite or alumina with the Cs aluminosilicates, and the spinel, uraninite and alumina merely crystallized. The nepheline calcine, however, did react with the Cs aluminosilicates. The products were the same as in the above-mentioned experiments with the mixed $CsAlSi_5O_{12}$ and nepheline calcines.

4. Discussion

A plot of the Cs extraction against the square root of leach time is shown in Fig. 3. This plot shows a clear linear dependence up to a leach time of about 50 days. However, the data are approximately consistent with a linear dependence for the entire 100 days and an appropriate straight-line fit of the data is shown.

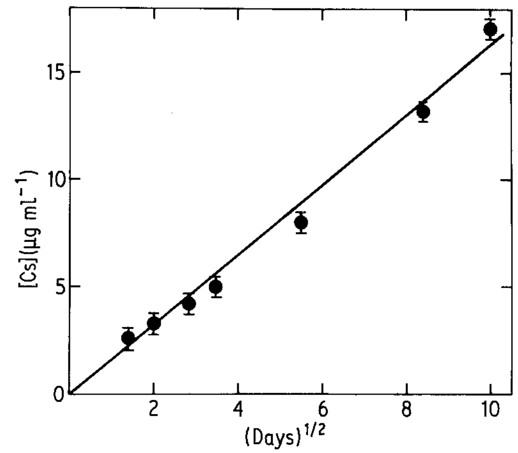

Figure 3 Cs extraction for $CsAlSi_5O_{12}$ as a function of the square root of leach time.

The dependence of pH of the Cs extraction in Fig. 2 is clearly based on sparse data. It might be argued that the experimental point at pH = 5.8 could be strongly perturbed by the dissolution of a very small fraction of fine particles adhering to the larger particles. However, in none of the time-dependence data, including that for pH = 5.8, was there any sign of "excess" dissolution from such a cause at small leaching times. No pH drift was noted either. Taking the results at face value, the Cs extraction varies as $[H^+]^n$, where $n \sim 0.36$ and the value of the exponent is in *severe* disagreement with the value of unity predicted by an ion-exchange model of Cs extraction.

No conclusions about the congruence of the dissolution process could be reached, partly because of the low solubility of silica in acid. However the principal problem was that, as previously mentioned, additional aluminosilicate phases were very likely present. Experimentally, for the pH = 1.02 measurements, the molar concentration of the Al present in the leaching solution was about 50% greater than the molar concentration of Cs.

The acid leach rates of $CsAlSi_5O_{12}$ and pollucite at 25° C and pH = 1.02 are now compared. The $CsAlSi_5O_{12}$ was a ceramic preparation with each granule consisting of a somewhat porous aggregate of micrometre-sized grains. The natural pollucite granules were derived from natural pollucite powder which was sintered at 1300° C and then crushed. This material was also somewhat porous (Adl *et al.* [13]). The BET areas of the pollucite and the $CsAlSi_5O_{12}$ were 0.08 and 0.18 m^2 g^{-1}, respectively. Though the absolute

TABLE III Cs leach rates* of pollucite and $CsAlSi_5O_{12}$ at 25° C

pH	pollucite	$CsAlSi_5O_{12}$
1.02	2.5×10^{-2}	6.5×10^{-4}
1.40	1.2×10^{-2}	5.0×10^{-4}
5.8	3.3×10^{-5} (see text)	4.9×10^{-5}
12.4	8.3×10^{-4}	4.7×10^{-3}

*Values are in g m^{-2} day^{-1} and are averages over the first 50 days of leaching. Surface areas are derived from BET measurements. If geometric surface areas were used, values for pollucite and $CsAlSi_5O_{12}$ would be increased by factors of 8 and 18, respectively.

values of such determinations may be somewhat controversial, relative values should be fairly reliable. Some Cs leach rates at different pH values are given in Table III. We conclude that at $pH = 1.02$ and 25° C, $CsAlSi_5O_{12}$ is approximately 30 times more resistant to Cs extraction than pollucite. At $pH = 1.40$, the factor is about 25. However, with increasing pH, in the acid range, the factor decreases and at $pH = 5.8$, the Cs extraction from pollucite is comparable with that from $CsAlSi_5O_{12}$ (using a value for pollucite which was derived from extrapolation of data obtained at lower pH values).

In approximately netural environments at 25° C, no firm deductions can be made, since the leach rates of both materials are minute. In principle, measurements might be made using finer powders. However, at least for pollucite (Adl *et al.* [13]), when experiments were tried with significantly finer powders, many problems arose associated with the particles failing to settle in reasonable times.

At about 95° C, this question could in part be answered using the well-known Soxhlet test. For pollucite, prepared by ceramic techniques, Strachan and Schulz [6] found $2.8 \pm 0.2\%$ mass loss in three days. The particle size was $-40 +$ 60 mesh. By the same methods, using similarly-sized particles, we found a 3-day mass loss of 0.2% for $CsAlSi_5O_{12}$. Experimental points were obtained (and fresh water used) after 1, 3, 7 and 14 days and the mass-loss results were essentially linear with time. Of course, this test only gives part of the answer because in neither case were monolithic granules, for which the surface area could be reliably measured, employed. For the $CsAlSi_5O_{12}$ preparation the deduced leach rate based on mass loss, and using the geometrical surface area, was about 0.1 g m^{-2} day^{-1}.

At 300° C, the data obtained in de-ionized water gave comparable Cs extraction figures for pollucite and $CsAlSi_5O_{12}$. The various chloride solutions gave considerably more Cs leaching than did de-ionized water and there was somewhat more fractional Cs extraction from the $CsAlSi_5O_{12}$ than the pollucite. However, the difference was only a factor of about two. Komarneni and White [17] have also reported on the action of de-ionized water and various chloride solutions on pollucite prepared by techniques similar to those employed in the present work. They used 50% larger particles but their leach times were twice those used here. Approximately similar results would have been expected. In the present work, however, the (unidentified) alteration product(s) formed on treatment of pollucite with $MgCl_2$ solution yielded X-ray powder diffraction lines at *d*-spacings of 1.13 and 0.463 nm, whereas Komarneni and White [17] reported the formation of chlorite. After treatment with 3M KCl, the $CsAlSi_5O_{12}$ preparation showed additional X-ray lines at 0.423, 0.380, 0.322 and 0.304 nm which we attribute to K-feldspar [18], together with an additional line at 0.84 nm. This latter line was observed after $CsAlSi_5O_{12}$ was treated with each of the chloride media. It is of course possible that the alteration products observed for the treated $CsAlSi_5O_{12}$ actually derived from the aluminosilicate impurities rather than from the $CsAlSi_5O_{12}$ itself.

The relative Cs extraction rates at $pH = 12.4$ for pollucite and $CsAlSi_5O_{12}$ are now considered. In experiments at 25° C with pollucite in which 3 M KCl, acidified with HCl, was used as the leachant, it was found that at constant pH, the presence of K^+ inhibited the Cs extraction considerably (Adl *et al.* [13]). This effect was not observed in similar experiments on $CsAlSi_5O_{12}$, so the slower dissolution rate of pollucite in dilute KOH relative to $CsAlSi_5O_{12}$ may in part be due to the presence of the K^+ ions.

The crystallization and compatibility studies are now briefly discussed. As expected from the results of Odoj *et al.* [19], $CsAlSi_5O_{12}$ is suitably refractory. The weight-loss of the pellet (Table II) on firing at 900° C is attributed principally to decomposition of residual nitrates as experience has shown that 600° C is not adequate to completely decompose $CsNO_3$ (see also [20]). Another possibility is that the pressed pellet may have absorbed H_2O from the air. Weight losses on heating beyond 900° C were minimal.

The formation of compounds less rich in SiO_2 than $CsAlSi_5O_{12}$ on firing at intermediate temperatures is not surprising. As an example, Buykx *et al.* [21] observed analogous results in preparing barium hollandite from a calcine.

No indications of incompatibility of either $CsAlSi_5O_{12}$ or pollucite were observed with respect to UO_2, (Fe, Ni) spinel, or Al_2O_3 at 1200° C, but the results were not definitive. Unlike the case of pollucite [22, 23] in which all the Al can be replaced by Fe^{3+}, no compound was formed in our experiments on calcines of $CsFeSi_5O_{12}$ stoichiometry fired at elevated temperatures. The compatibility studies of nepheline and $CsAlSi_5O_{12}$ very probably showed that a transient liquid-phase was present on heating at 1200° C.

To produce $CsAlSi_5O_{12}$ or pollucite from radioactive waste supernates several courses of action seem possible, though it would probably be simplest to sorb ^{137}Cs from a waste water, extract the ^{137}Cs, add this to appropriate quantities of $Al(NO_3)_3$ and $Ca(NO_3)_2$ solutions and SiO_2 sol and then dry, calcine, and crystallize/consolidate. However, for waste water with relatively low Na and high Cs content, it might be possible to virtually fully load a mordenite or chabazite with waste Cs, especially if a series of columns was employed. Sorption of ^{137}Cs on certain resins, followed by elution with formic acid, also promotes separation of Na and Cs [24]. In this case the Cs-loaded mordenite or chabazite could be fired directly at about 1000° C (depending on the Ca content) to produce crystalline pollucite and/or $CsAlSi_5O_{12}$.

Since ^{137}Cs is a β, γ emitter, radiation damage problems in $CsAlSi_5O_{12}$ appear to be minimal, though if solid-phase radiolysis [25] was important, long-term instability might result. There would be no variable-valence ions to mitigate [26] the $Cs \rightarrow Ba$ transmutation-induced instability in $CsAlSi_5O_{12}$. However, since, for ultimate disposal, only about 10^3 years is sufficient for ^{137}Cs to decay to negligible levels, complete reliance on the container for isolation from the biosphere would be feasible. The main advantage of a refractory, leach-resistant wasteform for ^{137}Cs would be for possible transportation accidents in the public domain. In this case the wasteform would presumably be freshly made so that impairment by radiation and transmutation would be small and recovery after a few days should present few difficulties.

5. Conclusions

$CsAlSi_5O_{12}$ is more leach-resistant than pollucite in acid media at 25° C and has comparable leach resistance to pollucite in near-neutral water or chloride solutions at 300° C and 30 MPa. The resistance to leaching at 25° C in strongly alkaline media of $CsAlSi_5O_{12}$ is slightly inferior to that of pollucite; this may be relevant to the encapsulation of Cs-bearing phases in cements which contain $Ca(OH)_2$.

A corollary of these results is that the occurrence of $CsAlSi_5O_{12}$ in pollucite preparations would have no significant deleterious effect on Cs extraction, except perhaps for strongly alkaline leaching media.

Kinetic data were obtained in strongly acid media at 25° C. The Cs extraction over the duration of the experiments was approximately proportional to the square root of the leaching time, suggesting the dissolution mechanism is controlled by the Cs diffusion coefficient in $CsAlSi_5O_{12}$. The Cs extraction rate at 25° C in acid varied as $[H^+]^{0.36}$.

A Soxhlet test on a ceramic preparation gave a leach rate of about $0.1\,g\,m^{-2}\,day^{-1}$, based on mass loss.

The addition of CaO, and to a lesser extent MgO, significantly lowered the crystallization temperature of $CsAlSi_5O_{12}$ from calcines and some limited compatibility data were obtained with regard to uraninite, alumina, spinel and nepheline.

Acknowledgements

This work was supported by the U.S. Department of Energy through the Rockwell Energy Systems Group under prime contract number DE-AC09-79ET41900. The experimental assistance of Mr S. D. Atkinson, Ms D. Wolfe-Confer, Ms B. Bodnar, and Dr D. K. Agrawal is appreciated. We thank Dr B. Scheetz and Dr S. Komarneni for helpful discussions.

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Received 17 June
and accepted 30 July 1981