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NUCLEAR WASTE IMMOBILIZATION

Progress Report to Lawrence Livermore Laboratory

As specified in Contract No. 6842009

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IMMOBILIZATION OF US DEFENSE NUCLEAR WASTES USING THE SYNROC PROCESS

1. INTRODUCTION

United States defense nuclear wastes are presently in tank storage, largely as sludges comprising Fe, Mn, Al, U and Na oxides and hydroxides, together with 0.5 to 5 percent of fission products and actinides (exclusive of uranium). The relative proportions of Al, Fe, Mn, Ni, U and Na in the sludges from different tanks vary considerably, except that (Fe + Al + Mn) are by far the major components and Fe is more abundant than Mn. Typical compositions of some calcined sludges from Savannah River are given in Table 1. In this paper we will briefly describe how the SYNROC process, utilizing straightforward technology, can be readily adapted to the problem of defense waste immobilization, yielding a dense, inert, ceramic waste-form, SYNROC-D.

This objective can be achieved as follows: about 30-50 wt.% of additional inert components ($TiO_2 + ZrO_2 + CaO \pm Al_2O_3 \pm SiO_2 \pm BaO$) would be intimately mixed with the sludges, followed by heating under controlled oxygen fugacity conditions to form a ceramic synthetic rock composed of a specific equilibrium mineral assemblage. This assemblage comprises the "original" SYNROC phases: zirconolite, perovskite, and hollandite, together with certain other refractory and leach-resistant minerals such as spinel, pseudobrookite, ilmenite and nepheline. In keeping with the SYNROC strategy, the immobilization of fission products and actinides would be achieved by incorporating them as dilute solid solutions forming integral parts of the crystal lattices of hollandite, zirconolite and perovskite. The additional thermodynamically-compatible phases (spinel etc.) serve to immobilize the "inert" sludge components, mainly Fe, Al, Mn, Ni and Na oxides.

The sodium contents of sludges influence the selection of an optimum immobilization assemblage. The sludges whose compositions are given in Table 1, were calcined after two or three stages of dispersal in water at ambient temperatures followed by centrifuging, filtering and drying. It seems possible that the sodium content could be substantially or greatly reduced by more intensive treatments - e.g. by washing in hot aqueous solutions containing ammonium or calcium ions. Accordingly, we will discuss two classes of processes - one designed to immobilize sludges containing "normal" amounts of sodium (cf. Table 1) and the other designed for otherwise similar sludges which are, however, strongly depleted

Table 1. Typical compositions of calcined sludges, Savannah River¹.

	High-alumina sludge ¹ 'H'-area	High-Fe sludge ¹ 'F'-area	Estimated average sludge ¹ composition for entire site
SiO ₂	-	2.2	0.9
UO ₂	3.5	3.7	3.4
Al ₂ O ₃	50.3	5.8	30.9
Fe ₂ O ₃	26.4	57.7	39.5
MnO	7.9	9.5	8.9
NiO	0.9	10.3	4.9
CaO	3.1	2.9	2.9
Na ₂ O	5.	5.	5.6
FP,A ²	3.0	3.0	3.0
Sum wt. %	100.	100.	100.

¹R. Garvin, pers. comm.

²Fission products plus actinides excluding U.

in sodium as a result of more efficient washing procedures. The processes which are discussed in the following sections are based upon the results of large numbers of experimental hot-pressing runs followed by detailed phase chemistry investigations using the electronprobe microanalyser and X-ray diffraction.

2. IMMOBILIZATION OF HIGH-SODIUM SLUDGES

(a) Introduction

There is a wide range of sodium-iron-titanate and sodium-aluminium-titanate compounds which can be synthesized. However, many of these are not very resistant to leaching. In order to immobilize sodium as a highly leach-resistant titanate, e.g. $\text{Na}(\text{Al}, \text{Fe})\text{Ti}_3\text{O}_8$, it would be necessary to add relatively large amounts of TiO_2 to the sludges. Whilst this is entirely feasible in principle, it encounters economic penalties. It would be preferable to immobilize sodium in a phase which did not require the addition of such a large quantity of inert additives.

After a review of possibilities, it was decided to immobilize the sodium in nepheline, $\text{NaAlSi}_3\text{O}_8$. This would require the addition of one mole of SiO_2 for each mole of Na_2O , and, in the iron-rich waste (Table 1, Column 2) a small amount of additional Al_2O_3 . Reconnaissance experiments demonstrated that nepheline is thermodynamically compatible with FeAl_2O_4 and Fe_2TiO_4 spinels, and also with perovskite and zirconolite, so that it would be possible to produce a modified SYNROC assemblage consisting of perovskite + zirconolite + Fe, Al-rich spinel + nepheline. Actually, this assemblage has close affinities with the earliest form of SYNROC studied (Ringwood, 1978) which contained kalsilite, KAlSi_3O_8 , as a separate phase.

In an earlier series of experiments, we investigated the partition of cesium between nepheline and a range of hollandite-type phases (Table 2). Cesium was found to display a strong preference for entering nepheline, which could accept more than 5 percent of Cs_2O in solid solution. Since the principal reason for including hollandite in earlier SYNROC formulations was to immobilize cesium, the presence of this mineral becomes redundant if the phase assemblage contains a substantial amount of nepheline. Accordingly, in SYNROC formulations for high-sodium defense wastes, it is not necessary to include BaO among the additives. (However, a small

Table 2. Partitioning of Cs between hollandite and nepheline in a SYNROC formulation incorporating high-Al sledge.

Sample in Pt capsule hot-pressed at 5kb, 1300°C (½ hr) then slow-cooled at pressure to 900°C over 1½ hrs.

	<u>Nepheline</u>	<u>Hollandite</u>
SiO ₂	37.8	-
TiO ₂	2.7	66.
ZrO ₂	0.4	1.2
UO ₂	-	0.1
Al ₂ O ₃	36.0	8.2
"FeO"	0.5	8.5
MnO	-	0.7
NiO	-	0.6
CaO	1.3	0.2
BaO	-	14.
Na ₂ O	17.3	1.1
Cs ₂ O	4.1	<.15
Sum	<u>100.1</u>	<u>99.3</u>

amount of BaO is necessarily introduced from the fission product component and this may result in the formation of a small amount of hollandite and/or BAIT, or even celsian, $\text{BaAl}_2\text{Si}_2\text{O}_8$).

It has been found advantageous to carry out the heat treatment of high-iron sludges under redox conditions which cause about half of the iron in the final SYNROC ceramic to occur in the ferric state (nickel and manganese remaining essentially divalent). This procedure reduces the amount of TiO_2 (or Al_2O_3) needed to immobilize $(\text{FeO} + \text{NiO} + \text{MnO})$, since it leads to the formation of an $(\text{Fe,Ni,Mn})^{2+}\text{Fe}_2^{3+}\text{O}_4$ component in the spinel phase.

The above objective can be readily achieved by carrying out the heat treatment at oxygen fugacities near the nickel-nickel oxide buffer. The most direct means of achieving this objective is to sinter or hot-press sludges plus additives in metallic nickel containers. Alternatively, sintering can be carried out in kilns in the presence of a gaseous atmosphere containing CO/CO_2 and/or $\text{H}_2/\text{H}_2\text{O}$ ratios appropriate to the Ni-NiO buffer. Under the same oxygen fugacity conditions, the SYNROC ceramics incorporating high-iron sludges are found to contain substantial amounts of ferric iron, whereas in SYNROC ceramics incorporating high-alumina sludges, most of the iron remains in the ferrous state. Thus, the entire compositional spectrum of sludges may be treated under essentially the same redox conditions - a factor which simplifies the processing equipment which is required.

(b) Experimental Procedures

Samples for experimental study were prepared by dissolving appropriate proportions of nitrates and carbonates of the required metals in water, admixing TiO_2 (in the form of ultrafine anatase) to form a slurry, evaporating to dryness, heating to decompose nitrates, and then calcining at 1000°C to form a homogeneous oxide mix of the desired composition. This material was then thoroughly reground and remixed under acetone in an agate mortar.

Samples were then recrystallized by hot-pressing using a solid media pressure apparatus as described by Green and Ringwood (1967). Most runs were carried out at temperatures between 1000 and 1300°C for periods of 1 to 3 hours at a confining pressure of 5 kilobars. Sample sizes were mostly in the range 50-100 mgm. In some cases, appropriate amounts of pure metallic iron or nickel

powders were added to the charges to produce the required oxidation state. In other cases, the redox state was controlled by encapsulating the sample in metallic iron, nickel or platinum containers during the hot-pressing operation. Runs carried out in iron capsules equilibrated at oxygen fugacities just below the Fe-FeO buffer, whilst runs in nickel capsules equilibrated just below the Ni-NiO buffer. (From extensive prior experience with this apparatus, it was known that runs in platinum capsules corresponded to oxygen fugacities very close to the Ni-NiO buffer). After completion of runs, the phase assemblages were identified by means of X-ray diffraction and individual phases were analyzed using an electronprobe microanalyzer.

The experimental program evolved via an iterative procedure. The sludge compositions on which the experimental program was based were those given in Table 1. Further additives were mixed with these sludges so that the bulk compositions corresponded to those of a mixture of perovskite + zirconolite + spinel + nepheline phases. These mixtures were then hot-pressed in runs carried out at 50°C intervals between 1000°C and 1300°C, and at several different oxygen fugacities (Fe, Ni and Pt capsules). Extensive electron microprobe analyses of these "first generation" runs provided considerable information on the natures of the phase assemblages, degree of equilibration and ranges of composition of individual minerals as a function of the run conditions. They confirmed that the sludges could be crystallized to form the above four phase assemblage: perovskite + zirconolite + spinel + nepheline. However, because of fine crystal size, which often made electron microprobe analysis difficult or impossible, and lack of complete equilibration in many runs, some important details of the mineral chemistry remained uncertain.

A second series of runs was then carried out using mineral compositional data obtained in the first series, but exploring the equilibria between only two of these minerals at a time, i.e. spinel + perovskite, spinel + zirconolite, spinel + nepheline, perovskite + zirconolite, perovskite + nepheline, zirconolite + nepheline. Many additional binary systems involving the equilibria of $\text{BaAlTi}_6\text{O}_{16}$, $\text{BaFeTi}_6\text{O}_{16}$, $\text{Ba}(\text{Fe}^{III}\text{Ti})\text{Ti}_6\text{O}_{16}$ hollandite, BAIT, ilmenite, corundum, rutile and pseudobrookite with the above phases were also studied. Partition equilibria of minor elements,

especially Cs, U and the rare earths among these phases were investigated. The advantage of this rather tedious procedure was that in these simpler binary systems, the minerals usually equilibrated more readily and crystallized more coarsely than in the first series of 4-phase runs, thereby permitting better quality electronprobe analyses and providing an improved understanding of the detailed mineral chemistry of the systems.

The information obtained from the first two series of runs finally led to the identification of a "preferred" mode of treatment, including definition of the optimum proportions of additives required for the successful immobilization of the sludge compositions in Table 1. These "preferred" treatment modes were then tested in a third series of runs, as described in the next section.

3. PREFERRED TREATMENT OF HIGH-SODIUM SLUDGES

(a) High-alumina sludge

The composition of this calcined sludge is given in Table 1, Column 1. The model sludge was intimately mixed with TiO_2 , ZrO_2 , CaO and SiO_2 in the proportions given in Table 3. These correspond to a mixture of 67 parts of volatile-free sludge to 33 parts of total additives. The mixture was then hot-pressed at 5 kbar at several temperatures between 1000°C and 1300°C in Pt, Fe and Ni capsules. The solidus appeared to be around 1150 – 1200°C on the basis of textural interpretation. At temperatures between 1100° and 1200°C the mixture crystallized completely to an assemblage of hercynite spinel (54 wt.%), zirconolite (16%), perovskite (13%) and nepheline (16%). (These proportions were estimated on the basis of microprobe data). Below 1100°C , evidence of disequilibrium was indicated. In runs between 1100 – 1200°C the samples were mechanically strong "synthetic rocks", devoid of porosity, with crystal sizes mainly between 2 and 10 microns.

The compositions of typical coexisting minerals for runs carried out in iron capsules are given in Table 3. At the redox conditions imposed by these capsules, most of the NiO^1 in the charge was reduced to the metallic state, forming an Ni-Fe alloy. A second series of runs in nickel capsules gave essentially similar mineral compositions, except that nickel oxide was not reduced, and the hercynite contained a few percent of NiO. The mineral

Table 3. Immobilization of high-Al sludges.

	High-Al Sludge Calcine	Inert Additives
SiO ₂	-	6.5
TiO ₂	-	16.7
ZrO ₂	-	4.2
UO ₂	2.3	-
Al ₂ O ₃	33.8	-
Fe ₂ O ₃	17.7	-
MnO	5.3	-
NiO	0.6	-
CaO	2.1	5.5
Na ₂ O	3.4	-
FP, A ¹	2.	-
Sum wt. %	67.	33.

Typical Examples of Coexisting Minerals²

	Zirconolite	Perovskite	Hercynite Spinel	Nepheline
Estimated proportions, wt. %	16	13	55	16
SiO ₂	-	-	-	41.5
TiO ₂	30.1	53.2	5.8	0.2
ZrO ₂	38.5	0.7	0.3	-
UO ₂	14.2	4.8	-	-
Al ₂ O ₃	1.1	0.3	48.3	35.9
FeO ³	4.2	2.4	37.4	0.8
MnO	0.9	0.7	7.2	0.2
NiO	-	-	0.4	-
CaO	12.5	38.1	-	-
Na ₂ O	0.4	-	-	21.5
Sum wt. %	101.9	100.2	99.4	100.1

¹Fission products plus actinides excluding U.²Run conditions: Fe capsule, 5 kb, 1200°C, 1 hr.³Total iron assumed as FeO.

Table 4. Immobilization of high-Fe sludges.

	High-Fe Sludge Calcine	Inert Additives
SiO ₂	1.4	4.8
TiO ₂	-	16.8
ZrO ₂	-	4.0
UO ₂	2.4	-
Al ₂ O ₃	3.7	5.4
Fe ₂ O ₃	36.8	-
MnO	6.1	-
NiO	6.6	-
CaO	1.9	5.0
Na ₂ O	3.2	-
FP, A ¹	2.	-
Sum wt. %	64.	36.

Typical Examples of Coexisting Minerals²

	Zirconolite	Perovskite	Ferrite Spinel	Nepheline
Estimated proportions, wt. %	15	11	59	15
SiO ₂	-	-	-	40.6
TiO ₂	35.1	52.4	7.9	0.5
ZrO ₂	25.2	1.4	-	-
UO ₂	15.5	2.6	-	-
Al ₂ O ₃	0.4	1.5	8.1	34.4
Fe ₂ O ₃	7.8 ³	1.6 ³	43.5	5.0 ³
FeO	-	-	20.7	-
MnO	1.8	0.8	9.0	-
NiO	-	0.2	9.7	-
CaO	14.6	39.8	-	-
Na ₂ O	0.2	-	-	20.1
Sum wt. %	100.6	100.3	98.9	100.7

¹Fission products plus actinides excluding U.²Run conditions: Pt capsule, 5 kbar, 1150°, 1 hr.³Total iron assumed as Fe₂O₃.

lized in the ferrous state, irrespective of variations in oxygen fugacities between the Fe-FeO and Ni-NiO buffers

(b) High-iron Sludge

The composition of this calcined sludge is given in Table 1, Column 2. The model sludge was intimately mixed with TiO_2 , ZrO_2 , CaO , Al_2O_3^* and SiO_2 in the proportions given in Table 4. These correspond to a mixture of 64 parts of dried sludge to 36 parts of total additives. The mixture was then hot-pressed at several temperatures between 1000° and 1300°C in Ni, Pt and Fe capsules. The solidus appeared to lie between 1150° - 1200°C on the basis of textural interpretation. At temperatures between 1100° and 1200°C , the mixture crystallized dominantly to an assemblage estimated from microprobe data to comprise ferrite spinel (58 wt.%), zirconolite (15%), perovskite (11%) and nepheline (15%). Below 1100°C , evidence of disequilibrium was indicated. In runs between 1100° and 1200°C , the samples were recovered as mechanically strong synthetic rocks, devoid of porosity and with crystal sizes dominantly between 2 and 10 microns, although spinel grains may be much larger ($\sim 50\mu\text{m}$).

The compositions of typical coexisting minerals for runs carried out in platinum capsules are given in Table 4. Similar results were obtained in nickel capsules. However, the use of iron capsules caused reduction of most of the NiO and some FeO in the charge to nickel-iron alloys. Thus, the preferred redox state for heat treating the high-iron sludges is near the Ni-NiO buffer. It is interesting that at this redox state, about half of the total iron is present in the ferric state. This contrasts with the case for high-Al sludges where nearly all the iron remained in the ferrous state at this redox state. The differing behaviour is caused by the effect of compositional differences between the sludges on the respective thermodynamic activities of FeO and Fe_2O_3 . This is a satisfying result in terms of process chemistry since the entire range of sludges may then be treated under similar redox conditions, in each case leading to the formation of an optimum mineral assemblage.

*Alternatively, the small amount of extra Al_2O_3 required can be supplied by mixing in some high-alumina sludge.

(c) Average Savannah River Sludge

The composition of the average calcined sludge is given in Table 1, Column 3. The sludge was intimately mixed with TiO_2 , ZrO_2 , CaO and SiO_2 in the proportions given in Table 5. These correspond to 69 parts of dried sludge to 31 parts of total additives. This sample was also doped with 1-2 percent of Sm_2O_3 . The mixture was then hot-pressed at 5 kbar at 1100°C , 1150°C and 1200°C in Ni capsules in runs of 1-3 hours duration. As might be expected, the behaviour was intermediate between those of the high-Al and high-Fe sludges. The solidus was estimated to lie between 1150 - 1200°C . The mixture crystallized dominantly to an assemblage estimated as spinel (53 wt.%), zirconolite (16%), perovskite (11%) and nepheline (18%). The samples were recovered as mechanically strong, synthetic rocks devoid of porosity and with crystal sizes dominantly between 2 and $10\ \mu\text{m}$. The spinel phase formed in this series of experiments represented a complex solid solution $((\text{Fe}, \text{Ni}, \text{Mn})^{2+}(\text{Al}, \text{Fe})^{3+}_2\text{O}_4 - (\text{Fe}, \text{Ni}, \text{Mn})^{2+}_2\text{TiO}_4)$ between the ferrite- and hercynite-type spinels formed during the treatment of high-Fe and high-Al sludges respectively.

(d) Discussion

The experiments described above show that by the addition of 30-35 percent of $(\text{TiO}_2 + \text{ZrO}_2 + \text{CaO} + \text{SiO}_2)$ to 65-70 percent of dried sludge, followed by appropriate heat treatment, it is possible to convert the sludges into mechanically strong synthetic rocks composed of the minerals spinel + zirconolite + perovskite + nepheline. Despite the very wide range of chemical compositions between high-Al and high-Fe sludges, inspection of Tables 3, 4 and 5 show that the amounts and proportions of additives are similar in all these cases. Moreover, despite the wide range in Fe/Al ratios of the sludges, it is found that all sludges can be satisfactorily immobilized by heat-treatment under the same redox conditions (near the Ni-NiO buffer).

This is a most felicitous situation with respect to the development of a relatively simple and economically efficient industrial-scale process for treating the wastes (Section 7). To a large extent, it is a consequence of the fact that the principal inert components in the waste are oxides of Al, Fe, Mn and Ni. When heated under appropriate conditions, these components become immobilized in a suitably inert spinel-type mineral phase. Apart

Table 5. Immobilization of average sludge composition.

	Average Sludge Calcine	Inert Additives
SiO ₂	0.6	7.5
TiO ₂	-	15.0
ZrO ₂	-	4.0
UO ₂	2.3	-
Al ₂ O ₃	21.2	-
Fe ₂ O ₃	27.1	-
MnO	6.1	-
NiO	3.4	-
CaO	2.0	4.9
Na ₂ O	3.8	-
FP, A ¹	2.1	-
Sum wt. %	69.	31.

Typical Examples of Coexisting Phases²

	Zirconolite	Perovskite	Spinel	Nepheline
Estimated Proportions, wt. %	16	11	55	18
SiO ₂	-	-	-	41.0
TiO ₂	32.5	53.6	14.3	0.5
ZrO ₂	32.7	<.1	0.2	-
UO ₂	11.2	3.0	.1	-
Al ₂ O ₃	1.1	0.1	17.2	35.2
Fe ₂ O ₃	7.1 ³	2.7 ³	20.5	1.1 ³
Sm ₂ O ₃	2.5	6.8	-	-
FeO	-	-	31.0	-
MnO	0.9	<.3	10.8	-
NiO	2.1	0.2	5.7	-
CaO	9.8	34.1	0.2	0.8
Na ₂ O	0.7	<.5	<.1	21.4
Sum wt. %	100.6	100.5	99.9	100.1

¹Fission products plus actinides excluding U.²Experimental conditions: Ni capsule, 5 kb. 1150°C, 1 hr.
Starting material doped with 1-2% Sm₂O₃.³Total iron assumed as Fe₂O₃.

from a small amount of SiO_2 needed to immobilize sodium, the remaining additives TiO_2 , ZrO_2 , CaO (BaO) are dedicated primarily to the objective of immobilizing the very small proportion (0.5 to 5%) of fission products and actinides (exclusive of U) present in the waste. Thus, the basic SYNROC concept (Ringwood, 1978) according to which the fission products and actinide components of the wastes are immobilized by incorporating them as dilute solid solutions in titanate minerals (zirconolite and perovskite) is retained; the principal difference being that the large excess of "inert" components of the waste crystallize principally as thermodynamically compatible spinels and nepheline. The latter phase, in addition, provides a host for the small amount of ^{137}Cs present in the waste.

(e) Terminology

The first form of SYNROC which was developed (Ringwood, 1978) consisted of a mixture of titanate and silicate minerals (hollandite + zirconolite + perovskite + kalsilite + celsian) which was crystallized from the molten state. It is convenient to refer to this as SYNROC-A. The second modification, also directed at immobilization of civilian power reactor radwaste calcine was a simplified form, consisting only of titanate minerals - hollandite + zirconolite + perovskite (Ringwood et al., 1979a). This waste form is produced by solid-state recrystallization and is conveniently referred to as SYNROC-B. When about 10 percent of radwaste is incorporated, together with additional TiO_2 and Al_2O_3 in order to facilitate the entry of radwaste components into the titanate solid solutions, a slightly modified waste form is obtained which is preferred for immobilization of civilian power reactor wastes (Ringwood et al., 1979b, Table 2, Column 2). This will now be called SYNROC-C, the suffix referring to "civilian". The modified SYNROC form as described in this paper, aimed at immobilization of defense wastes may thus appropriately be referred to as SYNROC-D.

4. ALTERNATIVE PROCESS FOR TREATMENT OF HIGH SODIUM SLUDGES

We are presently investigating an alternative process for immobilizing sodium in defense waste sludges. In this variant, sodium is incorporated, not in nepheline, but in a NaNbO_3 component

which possesses the perovskite structure. The mineral "lueschite" is essentially composed of NaNbO_3 and occurs in the 1020 million year old Illimaussaq intrusion in Greenland. We have found that when Nb_2O_5 is added to sodium-bearing SYNROC formulations, a perovskite solid solution ($\text{CaTiO}_3\text{-NaNbO}_3$) is formed, in which sodium is firmly bound. The sodium perovskite phase is thermodynamically compatible with other SYNROC phases including hollandite, zirconolite and spinel phases. A substantial amount of Nb_2O_5 also enters zirconolite. It is important that the ratio of Nb_2O_5 to Na_2O should exceed unity, to prevent the formation of water-soluble Na_3NbO_4 .

Because of the comparatively high cost of Nb_2O_5 , this version of the SYNROC process would be more expensive than the previous one. On the other hand, because of the apparently higher stability of the perovskite ($\text{NaNbO}_3\text{-CaTiO}_3$) as compared to nepheline (NaAlSiO_4), and also because it permits cesium to be immobilized in the very stable hollandite phase ($8\text{BaAlTi}_6\text{O}_{16}$), this additional cost may be justified. Further studies of this variant are in progress, in particular its practicability for immobilizing sludges containing SiO_2 as a minor contaminant.

5. IMMOBILIZATION OF LOW-SODIUM SLUDGES

In this process, it is assumed that the sodium content of the (dried) sludge can be reduced to less than one weight percent by more intensive and efficient washing procedures, e.g. in hot aqueous solutions containing NH_4^+ and/or Ca^{2+} ions which can exchange with sodium ions.

The treatment of sludges of this type was described by Ringwood et al. (1979b) and Ringwood and Kesson (1979a,b). The sludge compositions were modelled by assuming them to be composed dominantly of a mixture of varying amounts of inert (I) components ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{MnO}$) with a minor nuclear (N) component comprised of fission products and actinide elements (excluding U). At the time this work was carried out, the detailed compositions of sludges as given in Table 1 of this paper were not available and it was not realized that the dried sludges sometimes contained large amounts of NiO and U_3O_8 . Fortunately, however, the process as developed did not require any modification in order to cope with these components.

In this modification of the SYNROC process the heat treatment of the sludges was carried out under controlled redox conditions, between the Fe-FeO and Ni-NiO oxygen fugacity buffers, so that nearly all iron and manganese were reduced to the divalent state, whilst nickel remained divalent. Accordingly, the divalent species Fe^{2+} , Mn^{2+} and Ni^{2+} could effectively be treated as a single component, in view of the generally similar crystal-chemical behaviour of these ions. Since $\text{Fe}^{2+} \gg (\text{Mn}^{2+} + \text{Ni}^{2+})$, it was necessary only to consider FeO as representing this component.

The compositions of sludges within and between tanks vary widely. With the option available of remixing sludges, any desired degree of bulk chemical uniformity could be achieved. Nevertheless, it is desirable to demonstrate that a single basic process can be applied to cover the entire compositional range. We will illustrate this by reference to the compositions given in Table 1, modified only by removal of sodium.

(a) Immobilization of High-Alumina Sludges

A typical composition of such a sludge is given in Table 1, Column 1. Except for sodium, the sludges would consist of 97 percent of inert (I) components and 3 percent of nuclear (N) components (fission products and actinides). About 30 wt. percent of the inert additives TiO_2 , ZrO_2 , BaO and CaO in appropriate proportions would be intimately mixed with the sludge. The mixture would be heated to remove volatiles and decompose nitrates. The resultant calcine would then be sintered or hot-pressed under reducing conditions at 1200-1300°C as described above to form a mechanically strong, dense SYNROC titanate ceramic comprised of the minerals: hollandite + zirconolite + perovskite + titaniferous hercynite (FeAl_2O_4). The bulk of the Al, Fe, Mn and Ni in the sludge is incorporated in the latter mineral which is by far the most abundant in the assemblage (typically about 60%). Depending upon small amounts of corundum and/or pseudobrookite solid solutions (Al_2TiO_5 - FeTi_2O_5) can also be formed. In the absence of SiO_2 , minor amounts of sodium can be incorporated in zirconolite, hollandite and perovskite. Alternatively, nepheline may be formed if sufficient SiO_2 is present.

Uranium is found to enter the zirconolite as a $\text{CaU}_2\text{Ti}_2\text{O}_7$ component and to a lesser degree the perovskite phase. Of the "nuclear component" amounting to some 3 percent, the rare earths and strontium

dominantly enter the perovskite phase whilst the small amount of cesium present enters the hollandite². Partitioning and immobilization of the remaining fission products and actinides between hollandite, perovskite and zirconolite phases follows the description given by Ringwood et al. (1979a,b).

(b) Immobilization of High-Iron Sludges

A typical composition of such a sludge is given in Table 1, Column 2. About 50 wt.percent of the inert additives TiO_2 , ZrO_2 , BaO and CaO in appropriate proportions would be intimately mixed with the sludge. After preliminary calcining, the mixture would be sintered or hot-pressed under reducing conditions as described above at $1200\text{--}1300^\circ\text{C}$ to form a mechanically strong, dense SYNROC titanate ceramic composed of the minerals: zirconolite + perovskite + BAIT^{***} + ulvospinel, Fe_2TiO_4 . The bulk of the Al, Fe, Mn and Ni in the sludge is incorporated in the latter mineral which is by far the most abundant in the assemblage. Depending upon the exact composition of the sludge, and the amount and proportion of added inert components, significant amounts of ilmenite, ferropseudo-brookite and Fe-rich hollandite can also be formed. The remaining elements are partitioned as in case (a).

An alternative procedure is to replace part of the added TiO_2 by Al_2O_3 . This leads to immobilization of $(\text{FeO} + \text{MnO} + \text{NiO})$ via the formation of hercynite $(\text{Fe,Mn,Ni})\text{Al}_2\text{O}_4$ instead of ulvospinel $(\text{Fe,Mn,Ni})_2\text{TiO}_4$. The logical means of adding required Al_2O_3

*Most of the cesium derived from the fission product component is present in the supernatant liquid in the tanks and only a small proportion (5 percent of the total) is adsorbed on the sludges after washing. It seems likely, therefore, that if the sodium content of the sludges can be reduced by a factor of 5 or so below the levels given in Table 3 by more efficient washing and/or cation exchange, the cesium content would likewise be reduced by at least a similar factor. Accordingly, the low-sodium sludges to be treated would probably contain only very small amounts of ^{137}Cs . The primary reason for adding BaO to the sludges was to form hollandite or BAIT phases which would serve to immobilize the cesium. It now seems that this might not be necessary, and that hollandite and/or BAIT could be omitted as major phases from the preferred SYNROC mineral assemblages without adverse effects. A small amount of these phases would, however, necessarily be present, because of the occurrence of barium as a fission product. Alternatively, in the presence of sufficient SiO_2 , celsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$) may be formed.

***"BAIT" is a complex barium-aluminium-iron titanate possessing the approximate composition $\text{BaAl}_2\text{Fe}_8\text{Ti}_{13}\text{O}_{38}$.

would be by mixing some high-alumina sludge ($\text{Al}_2\text{O}_3 \gg \text{Fe}$) with the high-iron sludge.

(c) Immobilization of Sludges Possessing Intermediate Composition

A sludge possessing intermediate amounts of iron and alumina as in Column 1 of Table 3 would be treated analogously to the two cases discussed above. The principal difference would be that in this case, two different spinel minerals would crystallize in equilibrium, one being dominantly composed of FeAl_2O_4 , hercynite, and the other of Fe_2TiO_4 , ulvospinel (Fig. 2). Alternatively, additional alumina could be introduced, replacing part of the TiO_2 , as in case (b) above, so that Fe, Mn, and Ni would be immobilized dominantly in a hercynite spinel solid solution $(\text{Fe,Mn,Ni})\text{Al}_2\text{O}_4$.

It is important to appreciate, in the operation of this process, that successful immobilization of the sludges and development of a satisfactory mineral assemblage is not critically sensitive to the proportions and amounts of additives. Thus, a given working formula of additives ($\text{TiO}_2 + \text{ZrO}_2 + \text{CaO} + \text{BaO}$) is capable of immobilizing sludges possessing wide ranges in composition. This situation is a consequence of (i) the small proportion of active nuclear components in the sludge which are to be immobilized as dilute solid solutions mainly in the perovskite and zirconolite phases and (ii) the fact that in the presence of added TiO_2 , the excess Al_2O_3 , FeO , MnO and NiO are capable of forming a wide range of stable minerals, all of which can be accommodated in successful SYNROC formulations.

6. DISTRIBUTION OF MINOR HLW COMPONENTS

After mixing with the additional components required for sludge immobilization, the calcine will contain only a small total amount (averaging about 2 percent) of fission products and actinides. The partition behaviour of these components among SYNROC phases have been discussed elsewhere (Ringwood, 1978; Ringwood et al., 1979a,b), but additional results relevant to immobilization of defense wastes have since been obtained. A summary of relevant information on partition of the fission products and actinide elements of Table 2, and of other processing contaminants, is given below.

Rare Earths and Trivalent Actinides (e.g. Am^{3+} , Pu^{3+})

In the earlier work describing partition behavior occurring during crystallization of SYNROC from a melt (Ripwood, 1978), the trivalent rare earths preferentially entered the zirconolite phase, apparently because this mineral was the first to crystallize. However, in all subsequent work where partitions occurred during subsolidus conditions, the rare earths were dominantly partitioned into the perovskite phase, mostly by factors in the vicinity of 3. It is expected that the trivalent actinides, possessing crystal chemical properties resembling the rare earths, will also be partitioned preferentially into perovskite, although a significant proportion would nevertheless enter zirconolite. Only very minor amounts of these elements enter other phases.

Uranium and Tetraivalent Actinides

These elements preferentially enter into solid solution in zirconolite although significant amounts also enter perovskite. The partition coefficients $K(^{238}\text{U})$ typically range from about 2 to 5. The lower values seem to reflect non-equilibrium distributions. Early-formed perovskites may incorporate substantial amounts of U; as crystallization proceeds, perovskite then reacts with additional ZrO_2 and TiO_2 to form zirconolite, but equilibrium redistribution of U is not always attained.

Molybdenum

At the Ni-NiO buffer, molybdenum occurs as Mo^{4+} and substitutes for Ti^{4+} in all titanate minerals, especially hollandite and rutile. It is important that heat treatment should not be carried out under strongly oxidizing conditions (e.g. in air). Under these conditions, Mo, Cr, S and other components are oxidized to higher valence states as Mo^{6+} , Cr^{6+} and S^{6+} . These tend to form soluble sodium salts (molybdates, chromates and sulphates) which also incorporate a substantial proportion of the available (minor) cesium present. Moreover, calcining in air converts ruthenium to RuO_4 , which is very volatile. Heat treatment under controlled redox conditions as advocated in the SYNROC process, eliminates this problem, because ruthenium then occurs in an involatile, reduced state (see below).

Antimony, Bismuth (Mercury), Palladium, Rhodium, Ruthenium
Technetium, Tellurium

These elements are reduced to the metallic state, usually alloying with substantial amounts of nickel.

Cesium, Rubidium, Sodium, Barium

These elements are partitioned dominantly in nepheline. Barium may crystallize also in accessory celsian, hollandite and/or BAIT. In the absence of nepheline (low sodium, low SiO_2 sludges) Cs, Rb and Ba are strongly partitioned into hollandite and BAIT phases.

Phosphorus

Under the redox conditions preferred for heat treatment, (Ni-NiO buffer) phosphorus crystallizes either as a Ba-Ca orthophosphate, or as a coexisting pair of orthophosphates. Our experiments indicate incomplete solid solution between Sr- and Ca-end-members, with a miscibility gap between approximately $\text{Ba}_{0.4}\text{Ca}_{1.6}(\text{PO}_4)_2$ and $\text{Ba}_{0.5}\text{Ca}_{2.5}(\text{PO}_4)_2$.

Silica

In the absence of substantial amounts of sodium, silica combines preferentially with BaO and Al_2O_3 to form celsian, $\text{BaAlSi}_3\text{O}_8$. However, in the presence of substantial or large amounts of sodium, silica occurs preferentially as nepheline, $\text{NaAlSi}_3\text{O}_8$.

Sulfur

Sulfates are reduced to sulfides, occurring predominantly as NiS.

Strontium

Sr^{2+} is strongly partitioned into perovskite. Smaller amounts are incorporated into zirconolite and hollandite. In the absence of perovskite, Sr is readily partitioned into zirconolite.

Summary

Experimental results described above show that all fission products and processing contaminants present in defense wastes after initial heat treatment and removal of volatiles can be incorporated in the preferred SYNROC mineral assemblage. Most of

these elements enter into dilute solid solutions of zirconium perovskite, and, to a lesser extent, nepheline. A small proportion of remaining elements, principally processing contaminants, crystallize as accessory phosphates, sulphides and metal alloys.

7. TECHNOLOGICAL ASPECTS

After removal of the sludges from tanks, washing, and blending, they would be dispersed and intimately mixed with the required additive components mainly ($\text{TiO}_2 + \text{ZrO}_2 + \text{CaO} \pm \text{SiO}_2$). It is essential that the final heat treatment be performed upon an extremely well-mixed oxide calcine, preferably homogeneous at the sub-micron scale. There are several well-known means of achieving this objective which do not need elaboration. One of these would entail slurrying of the washed sludges and introduction of additives in aqueous solutions, followed by hydrolysis, leading to co-precipitation of additives as hydroxides around sludge particles. After centrifuging, washing and drying, the SYNROC-D feedstock could then be devolatilized by heating to 600-800°C, for example, in a spray calciner. The exact composition of the additives would depend upon whether the sludge contained large or small amounts of sodium, as discussed in earlier sections.

Starting with a homogeneous SYNROC-D oxide mixture of required bulk composition, there are several alternative further courses of treatment which might be envisaged. The first, and simplest would be to sinter the SYNROC-D powder. We find that SYNROC-D oxide mixes can be readily sintered to form strong pellets or larger forms possessing low porosity when heated at 1100-1200°C in a controlled atmosphere. According to one variant of this approach, pellets of SYNROC-D would be formed in a continuous sintering process by passing through a stationary heated kiln at 1000-1200°C. The redox conditions within the kiln would be maintained near the Ni-NiO oxygen fugacity buffer by means of a controlled gas atmosphere. The pellets could then be encapsulated in a continuous metallic matrix of copper to provide a waste form possessing high mechanical strength, high thermal conductivity and high corrosion resistance. Techniques for incorporating ceramic pellets in metallic matrices have been developed by several groups and are discussed, for example, by Jardine and Steindler (1979). About 65 percent by volume of pellets can be incorporated into waste forms

of this kind.

This procedure appears to possess major economic and technological advantages over alternative proposals to incorporate the waste in borosilicate glasses. It is unlikely that under sustained production procedures, it would be feasible to incorporate more than 25-30 weight percent of dried sludge in borosilicate glasses. This may be compared with about 65-70 weight percent of calcined sludge which is immobilized in SYNROC-D. Actually, the advantages of the SYNROC waste forms are even greater because of their much higher density (average $\sim 4.1 \text{ g/cm}^3$) than glass ($\sim 3.0 \text{ g/cm}^3$). As a result of combining the effects of the two factors mentioned above, SYNROC-D is seen to be capable of immobilizing about 3.2 times more sludge per unit volume than borosilicate glass. With efficient washing procedures removing most sodium from the sludges, nepheline would become a very minor phase in the SYNROC-D mineralogy, and the immobilization capacity of SYNROC would rise to about 3.6 times that of glass. Making an allowance for a metal matrix (about 35% by volume) between SYNROC pellets would still leave an advantage of a factor of two. This can be expected to produce large reductions in processing, transport, storage and ultimate disposal costs for the SYNROC-D waste form, as compared to borosilicate glass. Moreover, the technology needed to produce sintered pellets and to incorporate them in metals appears to be far simpler than that required for glass production. In the immobilization of high-Fe sludges, it may prove desirable to incorporate additional Al_2O_3 in order to produce a preferred phase assemblage (see Section 3b). This is most easily achieved by admixing high-Al sludges. These aluminous sludges are thus potentially very desirable additives in the SYNROC process. On the other hand, in borosilicate glass manufacture, high-Al sludges generate refractory crystalline phases which cause serious problems by blocking melter outlet pipes etc. This high-Al content of these sludges is so undesirable that an additional costly processing step, involving washing in hot concentrated alkali solutions, has recently been proposed (Garvin, pers. comm.). Finally, in comparison with borosilicate glasses, the SYNROC-D waste form possesses major additional advantages including higher strength and ductility, high thermal conductivity, chemical compatibility with natural rock systems and impermeability to gases.

A variant of the above sintering process might aim to produce much larger integral sintered bodies, e.g. short cylinders which could be deposited in hollow steel cylinders and the relatively small proportion of remaining void space then filled with molten lead. Yet another variant which could be employed is cold isostatic pressing of large cylinders of SYNROC-D (mixed with some nickel powder), followed by sintering at 1100-1200°C at atmospheric pressure in a controlled atmosphere, to produce very strong integral bodies. Preliminary work by the Australian Atomic Energy Commission on this technique as applied to SYNROC-C has yielded a very promising product. An advantage of these variants, shared also with the processes described below, is that the SYNROC-D waste forms contain from 3 to 3.6 times the mass of waste per unit volume as does borosilicate glasses. The economic benefits of this situation have already been noted.

A more elaborate treatment would be to apply the technique of large-scale isostatic hot-pressing (Larker, 1978, 1979). The SYNROC-D oxide mixture, including a small amount of dispersed metallic nickel powder would be hot-pressed at 1100-1200°C in nickel canisters, as proposed for SYNROC-C by Ringwood et al. (1979a,b). This procedure would produce a mechanically-strong waste form possessing negligible porosity.

Although this requires a more elaborate technology than the sintering operations described above, the product may well be significantly superior in its properties to an extent which justifies the additional expense. There are two further advantages of hot-pressing. Firstly, the formation of crystalline SYNROC-D in its terminal state and final encapsulation and sealing in a metal capsule are performed in a single operation. Secondly, volatile components such as Cs, Ru, Na, Bi and Hg are quantitatively retained and immobilized by SYNROC-D minerals during the hot-pressing operation and become permanently incorporated in the lattices of component SYNROC minerals as described earlier. The technique of hot-pressing large samples (3 m long by 0.5 m diam.) under the required conditions has already been developed (ASEA, 1977; Larker, 1978) and appears to lend itself to operation via remote control in hot cells, being no more complex in its essentials than glass-making technology.

Finally, we consider the fate of cesium which is present primarily in the supernatant liquid in the tanks at Savannah River and Hanford. In the former installation, it is proposed to incorporate the cesium ultimately in a sodium-zeolite. This could be recycled in a highly dispersed form (as a sludge) and added to the SYNROC-D (high-sodium) oxide mix prior to final heat-treatment. It would form discrete crystals of Na,Cs-bearing nepheline and/or pollucite-type minerals within the SYNROC-D mineral assemblage.

At Hanford, most of the cesium has been separated from the supernatant liquid already and concentrated in cesium-rich solutions. We would propose that this cesium should be separately immobilized in a hollandite-type solid solution ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ - $\text{Cs}_2\text{Al}_2\text{Ti}_6\text{O}_{16}$) which has previously been demonstrated to display truly exceptional stability and resistance to leaching, as compared with silicate minerals such as pollucite, $\text{CsAlSi}_2\text{O}_6$ (Ringwood et al., 1978, 1979). We suggest that a similar procedure be followed at Savannah River. This topic will be the subject of a separate report.

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EFFECTS OF RADIATION ON SYNROC MINERALS

1. INTRODUCTION

Concern has frequently been expressed that the ability of SYNROC to retain radwaste will be adversely affected by accumulated radiation exposure. By far the most important source of lattice damage in SYNROC minerals would arise from recoil of the parent nucleus during alpha decays from actinide elements. The host minerals for these elements are zirconolite and perovskite.

A program to evaluate the effects of alpha damage on these minerals has commenced. A collection of natural zirconolites and perovskites of different ages and containing different amounts of U and Th is being assembled. The accumulated alpha damage received by these minerals can be compared with that received by the same minerals in SYNROC containing 10 percent of high level waste calcine. Samples of natural zirconolites and perovskites are being studied by X-ray diffraction and analysed for U, Th and Pb by isotope dilution, with this objective in mind.

2. X-RAY STUDIES

The first question to be asked is what is the effect of radiation damage on the crystal structures of zirconolite and perovskite? To answer this question a series of naturally occurring zirconolite specimens which have an accumulated alpha dose ranging from 5×10^{17} to 1×10^{20} alphas per gram have been examined. The uranium and thorium contents of all specimens were first determined by electron microprobe analyses after which they were investigated by X-ray diffraction methods applied to single crystals or powder.

The Kaiserstuhl (Germany) carbonatite complex contains traces of zirconolite in a late stage vein. The estimated age of these samples is 16 my. The grains of zirconolite vary in their U and Th contents from a low of 0.8% UO_2 , 1.7% ThO_2 to a high of 1.5% UO_2 , 2.9% ThO_2 . The age of SYNROC which would have received an alpha dose equivalent to the high U sample would be about 10^3 years. X-ray diffraction on powders and single crystals shows this zirconolite to be well-crystallized. The zirconolite structure is closely related to that of fluorite. The X-ray data for these samples show that the fluorite subcell reflections remain constant while the

reflections from the zirconolite superstructure decrease slightly in intensity with increasing alpha dose. This effect is especially noticeable at high 2θ values, where slight broadening of spots is also seen. Based on these observations, we would expect that the zirconolite superstructure lines would still be present at twice this alpha dose. This would correspond to a SYNROC age of 8×10^3 years. After annealing at 1200°C , a slight increase ($\sim 2\%$) in density is noted.

A small grain of zirconolite from Jacupiranga, Brazil, with an age of 133 my. contains 0.4% UO_2 and 6.6% ThO_2 . The cumulative alpha dose for this sample is 7.6×10^{18} alphas per gram, which corresponds to a SYNROC age of 4×10^5 years. Preliminary X-ray photographs from single crystal chips of the Brazilian zirconolite show numerous, quite sharp reflections, characteristic of a fluorite-type lattice. However, the zirconolite superstructure reflections have completely disappeared. Thus, it appears that the basic effect of that high radiation dose has been to cause a degree of disorder of the cations, leaving the fluorite-type anion sublattice essentially intact.

Several Russian zirconolite samples were also examined. Preliminary studies indicate an age of about 650 my. Single crystal oscillation and rotation X-ray photographs showed that they were largely metamict; however, a few faint elongated reflections could be seen. The strongest reflection occurs at approximately $3.0 \text{ \AA}$, and corresponds to the 111 reflection of the fluorite-type subcell. Taking the age as 650 my., it is found that this sample has accumulated a dose of 1.7×10^{19} alphas per gram. This is somewhat more than the total alpha dose received by SYNROC in 10^6 years. Thus, in order to cause zirconolite to become truly metamict, the alpha dose would need to exceed that received by SYNROC over this period.

Small samples of loparite, a perovskite mineral containing large amounts of cerium and niobium, have also been studied by X-ray and electronprobe. The samples come from the Lovozero alkaline massif of the Kola peninsula. Samples of loparite from this intrusion dated by Komlev et al. (1961) gave a lead isotopic age of 300 my. The U and Th contents of our samples range from $\text{U} = 700 \text{ ppm}$, $\text{Th} = 1300 \text{ ppm}$, to $\text{U} = 1600 \text{ ppm}$, $\text{Th} = 3400 \text{ ppm}$.

For an age of 300 my., an alpha dose of 1 to 2.3×10^{18} would have accumulated for these samples. The corresponding ages for

SYNROC at this dose would be 10^3 to 10^5 years. Powder X-ray photographs reveal that the loparite crystals have not suffered any perceptible radiation damage to their crystal structure. The powder lines are sharp, and at angles of high 2θ , the α_1 and α_2 peaks are clearly resolvable. Comparison of these X-ray observations with those on Kaiserstuhl zirconolite indicates that the perovskite mineral is even more resistant to radiation damage than zirconolite. On annealing loparite at 1200°C , a slight decrease in "d" spacings occurs, equivalent to an increase in density of 1.7%. This is quite a small change in volume in relation to the alpha dose received and further demonstrates the stability of perovskite to radiation damage.

3. ISOTOPIC STUDIES

At very high alpha dosage ($>2 \times 10^{19}$ alphas/gram) zirconolite becomes completely metamict. Three samples from Sri Lanka which have received alpha doses in excess of 1×10^{20} alphas per gram have been studied. This is more than twice the dose for 10^7 year old SYNROC. In fact, it would take SYNROC 750 my. to accumulate this high dose.

For all of the minerals studied, it is important to know how well they are able to retain HLW. This involves the resistance of the minerals to leaching and the retention of daughter products from alpha decay processes. To examine both of these aspects analyses have been conducted of two specimens of zirconolite from the gem gravels of Sri Lanka for U and Pb concentrations by isotope dilution, Pb isotopic composition, and Th concentration by electron microprobe. These samples should represent a severe test since the accumulated alpha dose is very high, the samples are metamict, and the minerals have been weathered out of their original matrix and deposited by stream sedimentation. As such, the samples have been subjected to extensive attack by groundwater.

The lead isotopic ages are given in Table 1. Sample 83800 has a relatively large uncertainty in the $^{207}\text{Pb}/^{206}\text{Pb}$ age because of a small amount of common lead in the sample. This specimen contains 18% ThO_2 , 1.8% UO_2 and 0.56% Pb.

TABLE I

LEAD ISOTOPIC AGES OF SRI LANKA ZIRCONOLITES

Sample Number	83800	B20392
$^{207}\text{Pb}/^{206}\text{Pb}$ age	570 ± 20	565 ± 3 m.y.
$^{207}\text{Pb}/^{235}\text{U}$ age	567 ± 5	560 ± 2 m.y.
$^{206}\text{Pb}/^{238}\text{U}$ age	567 ± 5	559 ± 2 m.y.

There is no detectable loss of any of these elements since the three calculated ages agree within error limits, and the Th content is appropriate to the measured $^{208}\text{Pb}/^{206}\text{Pb}$ and age of the sample.

Sample B20392 contains less common lead than 83800; the measured $^{206}\text{Pb}/^{204}\text{Pb}$ was 11,800. This produces a more precise $^{207}\text{Pb}/^{206}\text{Pb}$ age which is in excellent agreement with that obtained for sample 83800. The uranium-lead ages for this zirconolite are in excellent agreement, and are within error limits of the $^{207}/^{206}$ age. Uranium, thorium and lead concentrations are similar to sample 83800.

The concordance of lead ages for Sri Lankan zirconolites is far better than that normally obtained for zircon samples. It is believed that this is because the decay product, lead, can be readily accepted into the zirconolite structure, whereas it does not fit into the zircon lattice. A further proof of the ability of zirconolite to retain daughter products was provided by Blake and Smith (1913). They found a large amount of helium (equivalent to an "internal pressure" of 5 atmospheres) retained in Sri Lankan zirconolite. Their analysis corresponds to approximately 36% retention of the total helium produced over the crystal's lifetime. This is remarkable in view of the readiness with which helium diffuses through most glasses and silicate minerals.

Zirconolite is also found as small (30-100 micron) grains in the Jimberlana mafic complex in Western Australia, which is about 2500 my. old (Turek, 1966; Lovering, in preparation). Wark (personal communication) has studied several samples and carried out careful electronprobe analyses for U, Th and Pb. The grains range from Th 2.0%, U 0.59% to Th 8.38%, U 2.27%. Wark has shown that the lead abundances in these grains are closely consistent with those expected to result from radioactive decay of the contained U and Th in 2500 my. Since it is unlikely that these grains contain any

significant amount of common lead, thus implying closed system behaviour for U, Th and Pb over a period of 2560 my. More recently, Lovering (personal communication) has dated two Jimberlana zirconolite grains by ion microprobe. He obtained lead 206/207 ages of 2500 my., thus establishing the closed system behaviour. This is remarkable in view of the enormous amount of radiation damage (sometimes exceeding 3×10^{20} alphas/gram) received by these small grains and the demonstrated fact that water obtained access to the intrusion as shown by partial serpentization of olivines (Campbell, 1977).

4. CONCLUSION

Concern has been expressed in several quarters that the integrity of SYNROC as a waste form might be compromised by the effects of radiation damage on its constituent minerals. The evidence discussed herein effectively dispels that concern. Radiation damage to crystal lattices is caused dominantly by alpha emitters (actinide elements) present in zirconolite and perovskite phases. We have seen that the zirconolite phase in SYNROC containing 10% of HLW would require about 10^6 years before becoming completely metamict, i.e. losing the capacity to diffract X-rays. By this time, the alpha activity in SYNROC would have declined to a value smaller than that present in a natural uranium ore body. This level of activity can be considered effectively safe for a waste form buried in a suitable geological repository. Moreover, even when metamict, the zirconolite continues to demonstrate a remarkable capacity to immobilize U, Th and their decay daughter products. The isotopic measurements on Sri Lanka and Jimberlana zirconolites demonstrated that these metamict minerals had behaved as closed systems for U, Th and Pb for periods of 560 and 2500 million years respectively, despite intense radiation damage (SYNROC equivalent ages, $\approx 10^9$ years). Moreover, the Sri Lanka zirconolite was sufficiently "tight" to immobilize a considerable proportion of radiogenic helium, one of the most mobile of elements, for 560 million years. The data on perovskite are limited and more work remains to be done. Nevertheless, present results indicate that perovskites are even more resistant to radiation damage than zirconolite.

The suite of natural zirconolites and perovskites studied here have experienced complex geological histories, including elevated temperatures and pressures, contact with groundwaters,

weathering and erosion over periods hundreds or even thousands of times longer than are needed for decay of high level waste to safe levels. They have been subjected to a range of geochemical stresses, far more intense than are likely to be found in any geological waste repository. Despite this they have retained their waste elements (alpha emitters) quantitatively. These observations provide the strongest grounds for confidence that the integrity and safety of SYNROC as a waste-form will not be adversely affected by radiation damage before the high level wastes have decayed to safe levels. The kind of evidence which we have described is important in another context. It provides a means of demonstrating to the general public in a readily understandable way that safe immobilization of radioactive waste elements over periods which are enormously long in comparison with human experience can indeed be achieved. This factor is likely to exert a strong influence on public acceptability of the feasibility of waste disposal. It should be noted that borosilicate glass waste forms, preferred by the nuclear power establishment, are intrinsically incapable of providing this kind of reassurance.

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SAFE IMMOBILIZATION OF RADIOACTIVE CESIUM
AND STRONTIUM AT HANFORD HIGH STORAGE SITE

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Abstract

Public resistance to the development of civilian nuclear power reactors in part arises from a lack of confidence in the capability of the nuclear industry to safely dispose of high-level wastes. This paper proposes a small-scale public demonstration of waste-disposal; specifically the immobilization of highly toxic radioactive strontium and cesium presently in storage at the Hanford Reservation. The chemical engineering and technological aspects of this program are straightforward, and ultimate disposal could be achieved in 5 years, or considerably less. The final waste-form is uniquely suited to on-site burial at Hanford. Moreover, no extensive geological surveys and site-assessments would be required because the waste-form itself provides the major barrier preventing environmental contamination.

The waste-disposal program would utilise a modification of the SYNROC strategy. Radioactive cesium would be immobilized as a dilute solid solution forming an integral part of the crystal lattice of the mineral, barium-hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$). Radioactive strontium would be similarly immobilized in the mineral perovskite (CaTiO_3). Accelerated leaching tests have already demonstrated the remarkable capacity of these phases to immobilize cesium and strontium. They are literally millions of times more stable than the borosilicate glasses currently favoured for waste disposal. Moreover, natural mineral analogs of these two phases have survived in Nature for 20-1000 million years in conditions far more extreme than would be encountered in any proposed repository. These facts offer a means of demonstrating to society a high degree of confidence in the long-term integrity of the waste form.

Introduction

At Hanford Reservation, large proportions of the radioactive strontium and cesium have been removed from the high level wastes and concentrated in separate tanks. Most of the strontium is present in solution, principally as nitrate, whilst most of the cesium is present in solution as cesium carbonate (Reep, pers. comm.). Currently, strontium from the tanks is being converted to strontium fluoride (SrF_2) which is then sealed in stainless steel cylinders, whilst cesium is being converted to cesium chloride (CsCl) and also sealed in stainless steel cylinders. However, only a small proportion of the total strontium and cesium has been so treated.

Cesium chloride and strontium fluoride are far from being ideal waste forms, either for ultimate disposal or for use in other areas. Cesium chloride is an extremely soluble salt, whilst strontium fluoride has a significant solubility in water.

The immobilization of cesium and strontium in crystalline titanate minerals has previously been described by Ringwood et al. (1979a,b). When cesium is incorporated in solid solution within the crystal lattices of hollandite-type crystals possessing the formula $2\text{BaAl}_2\text{Si}_6\text{O}_{28}$, it is phenomenally resistant to leaching by ground water and to processes of ion exchange, far more so than any cesium-containing silicate mineral such as pollucite ($\text{CsAlSi}_2\text{O}_6$) which is the main source-mineral for cesium in the earth's crust. When cesium is incorporated into the hollandite lattice it is immobilized literally millions of times more securely than it would be in borosilicate glasses of the kind which are currently favoured for radwaste immobilization.

Experimental studies in our laboratory showed that a hollandite phase containing 1 to 2 percent of cesium was unaffected by leaching in 10% NaCl solution at 800°C , 1000 atmospheres for 24 hours, whilst only slight attack occurred at 900°C , 5000 atmospheres for a similar period (Ringwood et al., 1979a,b). The crystal-chemical reasons for this behaviour are fully understood (Ringwood et al., 1979b; Sinclair et al., 1979). Likewise, radioactive strontium can be incorporated in dilute solid solutions within the crystal lattice of the natural mineral perovskite, CaTiO_3 . When 1 to 2 percent of strontium was incorporated in this manner, it was found to be unaffected by leaching in 10% NaCl solution at 1000°C and at a pressure of 5000 atmospheres for 24 hours (Ringwood,

1979a,b). This degree of stability is truly remarkable. The results have been exploited for the immobilization of more complex radwaste compositions (including ^{137}Cs and ^{90}Sr) in the synthetic titanate rock, SYNROC.

It is clear from extensive experimental results obtained so far, that it would be readily possible to permanently immobilize radwaste cesium as a dilute solid solution in $\text{BaAlTi}_2\text{O}_{10}$ hollandite and radioactive strontium in dilute solid solution in a perovskite, either CaTiO_3 or SrTiO_3 , the latter being based on common nonradio-genic strontium (principally ^{88}Sr). Natural hollandite-type minerals (e.g. $\text{K}_2(\text{Al,Fe})_2\text{Ti}_6\text{O}_{16}$) are known to have survived in nature for periods exceeding 20 million years, whilst perovskites have remained stable in rocks over 1000 million years old under pressures, temperatures and leaching conditions far more intense than would be encountered in any radwaste repository. This behaviour provides the strongest grounds for confidence that these minerals could survive in a suitable repository for the vastly shorter period of about one thousand years necessary for decay of these radioactivities to safe levels.

Strontium-90 ultimately decays to zirconium. Provided the proportion of ^{90}Sr introduced into the perovskite were low (e.g. <2%), this transmutation is most unlikely to significantly destabilize the crystal lattice. Perovskite phases can tolerate a substantial degree of non-stoichiometry and zirconium is perfectly "at home" in the crystal lattice, as shown by the fact that the compound CaZrO_3 also has a perovskite structure. Thus, when ^{90}Sr is incorporated in perovskite, the resultant Zr atom produced by radioactive decay would need to migrate only a couple of Angstrom units in order to find a suitable lattice site. Similarly, ^{137}Cs ultimately decays to barium. But the cesium would already be replacing barium in the hollandite lattice so that the transmutation of cesium atoms occupying a few percent of the normal barium sites would not cause any significant problems. Moreover, the $\text{BaAl}_2\text{Ti}_2\text{O}_{10}$ hollandite lattice permits a wide degree of non-

*To put these results in perspective, it should be noted that most crustal rocks would melt in minutes under these same conditions, and likewise borosilicate glasses. In fact, borosilicate glasses were found to lose radwaste species, devitrify and disintegrate under comparatively mild leaching conditions (10% NaCl at 300-400°C, 1000 bars for 24 hrs. - Ringwood et al., 1979b).

stoichiometry (Quinby et al., 1978; Sinclair et al., 1976) which would facilitate retention of the barium daughter product resulting from radioactive decay of ^{137}Cs without significant damage to the hollandite lattice.

Technology

The techniques needed to incorporate radioactive $\text{Sr}(\text{NO}_3)_2$ and Cs_2CO_3 presently stored in the Hanford Tanks into the above phases would be relatively simple. Several alternative and well-established technologies are available. For example, appropriate quantities of $\text{Ca}(\text{NO}_3)_2$ or $\text{Sr}(\text{NO}_3)_2^*$ would be introduced into a batch of radioactive strontium nitrate solution. After evaporating down to a desired concentration, the required amount of very fine-grained TiO_2 (anatase) would be added and fully dispersed by agitation. The slurry would then be introduced into a spray calciner, heated to 800-1000°C and thereby calcined to form an intimate mixture of finely powdered oxides possessing perovskite stoichiometry $(\text{Ca},^{90}\text{Sr})\text{TiO}_3$. The powdered calcine thereby produced could be pelletized and sintered at high temperature to form pellets of $(\text{Ca},^{90}\text{Sr})\text{TiO}_3$ or of $(^{90}\text{Sr},^{90}\text{Sr})\text{TiO}_3$ containing about 2 percent or less of ^{90}Sr . Alternatively the oxide mixes could be hot-pressed using existing technology to form fully dense samples possessing any desired shape (Larker, 1979).

In the treatment of radioactive cesium wastes, $\text{Ba}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$ and TiO_2 (as anatase) would be added to a batch of radioactive $^{137}\text{Cs}_2\text{CO}_3$ solution in proportions required to obtain hollandite-type $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ - $\text{Cs}_2\text{Al}_2\text{Ti}_6\text{O}_{16}$ bulk compositions. The resultant agitated slurry would then be heat-treated using a similar method to that discussed above in the preparation of perovskite.

Alternative methods of obtaining fine-grained, homogeneous oxide mixtures of desired composition, for subsequent sintering or hot-pressing might be based on application of the urea coprecipitation process (Quinby, 1978) or the "sol-gel" process (Lackey et al., 1979).

That portion of the radioactive cesium at Hanford which has been converted to CsCl would need prior treatment before employing the above techniques. The simplest procedure would be to

*i.e. non-radioactive "common" strontium nitrate.

dissolve the cesium chloride in water and pass the solution through an appropriate ion exchanger, thereby transforming the cesium chloride to a carbonate, nitrate or hydroxide, which could be treated as described above for radioactive cesium carbonate.

Treatment of strontium already converted to SrF_2 would be slightly more complicated. However, the following reactions have been found to proceed readily to completion in the solid state at 1200-1300°C.

Analogous reactions can be written to produce related minerals of the chondrodite ($2\text{Mg}_2\text{SiO}_4 \cdot \text{MgF}_2$) family by varying the stoichiometry in obvious ways. (The other members of this family are norbergite $\text{Mg}_2\text{SiO}_4 \cdot \text{MgF}_2$, humite $3\text{Mg}_2\text{SiO}_4 \cdot \text{MgF}_2$ and clinohumite $4\text{Mg}_2\text{SiO}_4 \cdot \text{MgF}_2$).

The important fact is that $^{90}\text{SrF}_2$ can be completely reacted in a closed system to form a biminerallitic rock composed of perovskite plus, for example, chondrodite. Effectively, all of the strontium is partitioned into the perovskite, which, as already noted, is an extremely stable phase. Moreover, chondrodite and other members of this mineral family are also known to have survived in natural rock systems for periods exceeding one hundred million years.

In applying this process to immobilize $^{90}\text{SrF}_2$, additional common strontium oxide or calcium oxide plus titania would be added in equal molar proportions so that the $^{90}\text{SrTiO}_3$ component represented only a small proportion (e.g. <5 mol percent) of the ultimate perovskite solid solution. Thus, the bulk of the synthetic rock would be composed of perovskite, with a smaller proportion of, e.g. chondrodite.

The process would be accomplished by intimate mixing of components, pelletizing and sintering or hot-pressing at 1200-1300°C.

Final Disposal

Operation of the above processes would yield pellets, spherules or discrete blocks of perovskite and hollandite containing ^{90}Sr and ^{137}Cs firmly immobilized. I propose that these pellets,

spherules or blocks be mixed with metallic copper powder. The mixture of copper powder and synthetic minerals would then be cold-pressed, followed by sintering at 600-900°C to form a fully dense cermet composed of hollandite and/or perovskite pellets (or spherules, or blocks) dispersed within a continuous copper matrix. Other known techniques of producing the copper-titanate mineral cermet could also be employed, e.g. hot-pressing or impregnation with molten copper.

The resultant waste form would possess a truly outstanding degree of stability and integrity when buried in an appropriate geological repository. The observed long-term geologic stabilities of perovskite and hollandite-type minerals, combined with the experimental evidence of resistance to leaching and ion-exchange in aqueous solutions at very high pressures and temperatures provide a high degree of confidence that these minerals as waste forms, would survive in geologic environments for millions of years. This may be compared with the timescale of about 1000 years necessary for decay of ^{137}Cs and ^{90}Sr to safe levels.

The integrity of the waste form is further increased by the procedure of dispersing the titanate mineral pellets in a copper matrix. This provides a number of advantages, including mechanical strength, high thermal conductivity and thermodynamic compatibility with basaltic rocks. Native copper is known to have survived for over one billion years in the geochemical environment provided by basaltic rock systems. Thus, one might be confident that the copper matrix would survive for a very long period if buried in a repository in basaltic rocks at Hanford (Fyfe, 1977).

Socio-political Aspects

At present the people of the United States are strongly polarized on the question of disposal of nuclear wastes. Because of inadequate research and development on waste forms other than glass during the last 30 years, and widespread uncertainties about the integrity of glass, there is a serious lack of public confidence that safe disposal of radioactive wastes over long timescales can be firmly guaranteed. Unless confidence is restored, this may prejudice the very future of the nuclear power industry.

The separated radioactive strontium and cesium at Hanford amount to very small, almost trivial, volumes of toxic material.

However, because these isotopes are responsible for the generation of a large proportion of the total heat produced by normal nuclear reactor wastes during the first 1000 years, they are of strategic importance in any disposal program.

I have shown above that these particular isotopes could be safely immobilized in synthetic titanate minerals which would be incorporated into a copper cermet. This waste form would provide an extreme degree of safety and redundancy which should fully satisfy the very genuine anxieties which exist within the community on this issue. The period for which safe immobilization is required is less than 1000 years. The volumes of waste concerned are very small and, because of their chemical purity and simplicity, the chemical engineering processes needed to immobilize these wastes, as described above, are also relatively simple and not excessively expensive. The combination of small volumes and simplicity in processing means that the required programme of research and development, followed by plant construction, and incorporation of the wastes in titanate-copper cermets could be carried to completion within a short period - in my opinion, less than five years (much less if necessary). The products could safely (and appropriately) be buried in repositories within basaltic rocks on the Hanford Reservation.

Successful execution of this project would demonstrate to the nation and to the world that the nuclear waste disposal problem can indeed be safely solved. It is just possible that this demonstration could provide the confidence necessary for the survival of the nuclear industry. I propose that a crash program be initiated to immobilize the Hanford radioactive strontium and cesium wastes as described above.

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The crystal structure and chemistry of a barium-
titanate hollandite-type phase

by

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Abstract

The crystal structure of $(\text{Ba}_{.98}\text{Ca}_{.03}\text{Sr}_{.02})(\text{Al}_{1.10}\text{Ni}_{.48}\text{Ti}_{6.4})\text{O}_{16}$ hollandite has been refined by the full-matrix least-squares method using 624 three-dimensional reflections to a final R value of 0.059 for the 22 variables involved. The data were collected on a four-circle diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation. The structure is tetragonal, space group $I4/m$ with cell dimensions of $a = 10.039(1)$, $c = 2.943(1)\text{\AA}$, and $Z = 2$. Refinement of the structure with the large A cations on the 2(b) site $(0,0,\frac{1}{2})$ resulted in an unacceptably high residual. This atom was displaced to site 4(e) $(0,0,\pm z)$ with $z = 0.3845(7)$, as indicated by the difference electron density map and refinement proceeded satisfactorily.

There are now two A-O(1) bond distances, four each of $2.787(3)$ and $3.126(3)\text{\AA}$ respectively. The O(1) atoms form a cage-like framework around the 4(e) site which effectively immobilize large A atoms such as Cs, K, Rb and Ba. The large thermal parameter U_{33} ($.054(2)$) of the A atom and significant residual ($4e/\text{\AA}^3$) at $(0,0,0.31)$ and ($2.2e/\text{\AA}^3$) at $(0,0,\frac{1}{2})$ on the final difference fourier map suggests additional position disorder such that the refined value is the most probable over a range.

Results of solid state preparations of $\text{Ba}_x\text{Al}_{2x}\text{-Ti}_{8-2x}\text{O}_{16}$ hollandites with different compositions are presented. These show a large range of x , varying from 0.3-1.2.

Introduction

$\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ (ideal formula) is the most abundant phase used in SYNROC, a synthetic rock developed for nuclear waste immobilization (Ringwood, 1978). This mineral possesses the tetragonal hollandite structure and is capable of a large number of substitutions of cations with different radii and charge. Ringwood, Kesson, Ware, Hibberson and Major (1979a) have shown, through accelerated leaching tests, that this compound is extremely stable and strongly resists attack by aqueous sodium chloride solutions at elevated pressures and temperatures.

The crystal structure of natural hollandite $\text{BaMn}_8\text{O}_{16}$ was first studied by Byström and Byström (1950). They found the structure to consist of an octahedral framework forming large channels parallel to the c-axis. It is within these channels that large cations can reside, thus stabilizing the structure (Bayer and Hoffman, 1966). Dryden and Wadsley (1958) successfully synthesized a non-stoichiometric phase $\text{Ba}_x(\text{Ti}_{8-x}\text{Mg}_x)\text{O}_{16}$ possessing this tetragonal hollandite structure. These workers found that the hollandite structure was able to accommodate a range of compositions with x varying from 0.6-1.14. The range for the hollandite lattice was studied further by Bayer and Hoffman (1966). They showed the large cations, Cs^+ , K^+ and Rb^+ , and many smaller ions could combine to form the tetragonal hollandite-type structure.

Although the main features in all previous structural analyses of the tetragonal hollandite have never been in doubt, a refinement using modern methods has been desirable. Both previous structure determinations resulted in high R values and neither individual temperature factors nor final difference electron density maps appear to have been calculated. Recently, Cadée and Verschuur (1978) synthesized several compounds with hollandite stoichiometry. A single crystal analysis showed that these phases have a small monoclinic distortion of the tetragonal lattice. In the course of structure solution the A cation position was moved from the expected special position 2(b) (0,0,0) to special position 4(e) (0, $\frac{1}{2}$,0), decreasing the co-ordination number to 10.

In view of the important potential application of this phase for the immobilization of radioactive elements in high level nuclear wastes and the need for a fundamental understanding of its properties and behaviour, a detailed crystal structure analysis of the SYNROC hollandite-type phase was carried out.

Experimental

The crystals were synthesized from a mixture of SYNROC-A components (Ringwood et al., 1979a,b). These components were sealed in a Ni capsule and pressurized to 0.5 GPa in a piston-cylinder apparatus (Boyd and England, 1960). Temperature was increased to 1300°C, held for one hour and then slowly lowered at 3°C/min

to 1150°C, and then at 30°C/min to room temperature. After removing the charge, the large hollandite-type crystals (4.5 x .5 x 1mm) were easily visible amongst the other phases. The crystals are acicular, cleaving along the long dimension, i.e. parallel to the c-axis. They are birefringent, exhibiting a brilliant green colour when viewed with transmitted light. Some crystals are also pleochroic. Most of the crystals examined showed twinning and/or multiple fragments. Splitting of reflections was apparent on zero or upper level Weissenberg photographs. It was not until a very small fragment (<100 microns) was chosen that the splitting disappeared.

Powder samples of the hollandite phase with differing stoichiometries ranging from $\text{Ba}_{0.6}\text{Al}_{1.2}\text{Ti}_{6.8}\text{O}_{16}$ to $\text{Ba}_{1.6}\text{Al}_{3.2}\text{Ti}_{4.8}\text{O}_{16}$ were also prepared. $\text{Ba}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$ and TiO_2 (anatase) were thoroughly mixed in the desired ratios in an agate mortar. The mixture was sintered in air at 1000°C for 1 hr to decompose the nitrates. The resulting mixture was reground and sealed in a Pt capsule. The sample was then reacted under solidus conditions at 0.5 GPa pressure and 1400°C temperature for 0.5 hr in a piston-cylinder apparatus. The products were examined by electron microprobe and powder X-ray techniques. The electron microprobe analyses were carried out by Mr. N. Ware and are presented in Table 1.

Crystal-Structure Analysis

Several crystals were mounted on quartz glass fibres and preliminary Weissenberg (Cu $K\alpha$ /Mo $K\alpha$ radiation) and Precession (Mo $K\alpha$ radiation) photographs were taken. Exposure of the $hk(0-2)$ and $h(0-1)l$ layers, respectively showed a tetragonal cell with Laue symmetry $4/m$ and revealed systematic absences for reflections of the type $h + k + l = 2n + 1$, confirming the space group as $I4/m$, $I\bar{4}$, or $I4$. Long exposure rotation photographs (>100 hrs) taken with c -axis as rotation axis showed extra diffuse spectra between the Bragg layer lines. Reflections at $2 \times c$ as found for $BaFeMn_7O_{16}$ (Mukherjee, 1964), $3xc$ for $Ba_{.65}Ru_{2.7}Cr_{1.3}O_8$ (Cadée and Prodan, 1979) or $2xa$ and c for redlejeite $(Mg,Ca,OH,H_2O)_2(Ti_{6.9}Cr_{1.5}Si_{0.5})_3O_{16}$ (Strunz, 1963) and $(K,Ba)(AlTi)_8O_{16}$ (Bayer and Hoffman, 1966) were not present.

The crystal chosen for data collection was irregular in shape with approximate dimensions of $0.100 \times 0.060 \times 0.025$ mm (elongated in the c -direction). The crystal was mounted onto a computer controlled fully automatic Picker FACS-1 four circle diffractometer, with the c -axis approximately parallel to the ϕ -axis of the diffractometer. Unit-cell dimensions and crystal orientation matrix were obtained by least-squares refinement of the setting angles of twelve carefully centred reflections having 2θ values between 50° and 60° using $MoK\alpha_1$ radiation ($\lambda = 0.70926\text{\AA}$) reflected from a graphite-crystal monochromator. Crystal data are given in Table 2.

Intensity data were measured by the θ - 2θ continuous scan technique using a scan speed by 2°min^{-1} (2θ) and range from 0.8° below the $K\alpha_1$ to 0.8° above the $K\alpha_2$ peak for the reflection concerned. Stationary background counts of 20' duration were made at each extreme of the scan range and were assumed to vary linearly between these extremes. Intensities of three standard reflections (600, 060, 002) were monitored regularly during data collection in order to check crystal and electronic stability. No significant variations in their intensities were observed throughout the course of the experiment. Intensities were collected for reflections having 2θ values between 3 and 120° and spanning one unique octant of reciprocal space. Of the 1248 reflections measured (excluding standards), 734 (59%) for which $I > 3\sigma(I)$ were accepted as being significantly above background. After sorting and averaging only the unique 624 reflections were used in subsequent calculations. These were reduced to values of F in the usual way and corrected for absorption effects. The statistical discrepancy value for this data set $R_s (= \sum |F_o| / \sum |F_o|)$, where σ is the error contribution to $|F_o|$ from counting statistics alone) is 0.040. Transmission factors for F_o , calculated by the analytical method of De Meulenaer and Tompa (1965), varied from 0.825 to 0.903. Extinction effects were not observed as there were no intense low angle reflections, consequently no correction was made for these effects.

Structure Solution and Refinement

Scattering factors for neutral atoms were taken from International Tables for X-ray Crystallography (1974).

Two composite curves were calculated using the Al/Ni ratio and the Ca/Zr composition obtained from probe results (see analysis 1, Table 1).

The refinement was carried out using the full-matrix least squares program SFLS which minimizes the function $\sum w(|F_O| - k|F_C|)^2$ where k is an overall scale factor, and w is the weight of an observation taken as unity in the initial stages and later assumed the form $w(hkl) = 1/\sigma^2$ where $\sigma^2 = [\sigma_1^2 + .25(0.03(F_O))^2]^{1/2}$.

Initial atomic co-ordinates from Byström and Byström (1950) were used in the refinement in space group $I4/m$. After several cycles of refinement, the discrepancy factor R (where $R = \sum ||F_O| - k|F_C|| / \sum |F_O|$) remained at 0.20 with little shift from the initial atomic co-ordinates. Interestingly, both previous structural analyses, Byström and Byström (1950) and Dryden and Wadsley (1958), reported high R values of 0.19 and 0.21 respectively, at the completion of structure solution.

At this stage, a 3-dimensional fourier map was calculated for the unique portion of the unit cell, using the phases calculated from the least squares refinement. This clearly showed an elongated region of electron density on the c -axis at the Ba position on $(00\frac{1}{2})$. A second difference fourier was calculated using only phases derived from the titanium and the two oxygen positions. This again showed a region of electron density elongated along the c -axis and centred around $00\frac{1}{2}$, however, we could now resolve two peaks, symmetrically related at $(0,0,\pm z)$. These 4(c) positions, rather than 2(b) sites, were assigned to the Ba atom which was then

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allocated an occupancy such that the contribution to the scattering was maintained at 0.98 Ba atoms per cell. Refinement using this model reduced the value of R to 0.11 using isotropic temperature factors and 0.062 with the introduction of anisotropic temperature factors.

Occupancies for Ba and Ti and for the composites Al/Ni, Ca/Zr, were refined separately. Although the occupancies changed only slightly the R value decreased to 0.059 and the weighted value R_w to 0.058 (where $R_w = [\sum w(|F_o| - k|F_c|)^2 / \sum w|F_o|^2]^{1/2}$). An analysis of $w(|F_o| - |F_c|)^2$ vs. F_o and $\sin \theta/\lambda$ showed no systematic trends indicating an adequate weighting scheme. The standard deviation of an observation of unit weight was 1.45.

A difference fourier map calculated at this stage showed a residual at (0,0,0.31) of $4e/\text{\AA}^3$ which is about $3e/\text{\AA}^3$ above general background and at (0,0, $\frac{1}{2}$) of $2.2e/\text{\AA}^3$. Other refinements in space group I4 resulted in increased R values with retention of the mirror symmetry especially about (h,k, $\frac{1}{2}$). This suggests I4/m as the correct space group. Final atomic parameters are presented in Table 3*. Bond lengths and angles are shown in Table 4.

*A list of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. . Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester, CH1 2HU, England.

The ANUCRYS Structure Determination Package (Whimp, Taylor, McLaughlin and Kelly, 1977) as implemented on the UNIVAC 1100/42 computer at the Australian National University, was used throughout the structure solution.

Discussion

The structure determined from this study (Figs. 1 and 2) consists of a framework of BO_6 octahedra similar to that reported by Byström and Byström (1950) and Dryden and Wadsley (1958), forming channels running parallel to the c-axis.

These authors placed the large A atoms on special position 2(b) $(0,0,\frac{1}{2})$ within the channels. In our present study we have shown that the A atoms are incorrectly located on this site. The correct position for these cations is on special position 4(c) at $(0,0,1z)$ with $z = 0.3845(7)$, the mirror symmetry being preserved by partial occupancy of the two new sites. This positional shift for the A cation was also found from an X-ray study of a monoclinic hollandite by Cadée and Verschoor (1978) and a small shift $(22\% \times c)$ was proposed for the tetragonal hollandite $\text{K}_{1.54}\text{Mg}_{0.77}\text{Ti}_{7.23}\text{O}_{16}$ by Beyeler (1976) from an analysis of the supplementary diffuse spectra. The A atom in this position is enclosed by eight O1 atoms, four at a distance of $2.787 \overset{\text{O}}{\text{\AA}}$ and four at a distance of $3.126 \overset{\text{O}}{\text{\AA}}$. Four more O2 atoms surround the A cation in the $z = \frac{1}{2}$ plane, however, these lie at a greater distance of $3.397 \overset{\text{O}}{\text{\AA}}$.

The coordination of the A cation in the channels is to be essentially eight-fold, although the four O2 atoms will exert a small attractive force since they occupy spaces between the O1 framework in a different plane.

For the A atoms to move along these channels involves passing through the square planar arrangement of O1 atoms above or below the 4(e) site. The size of the window defined by this oxygen framework and through which the Ba ions would have to pass is much smaller (half the diagonal distance across the window is $2.55 \text{ \AA}$) than the sum of barium plus oxygen ionic radii ($2.82 \text{ \AA}$ Shannan and Prewitt, 1969). This "cage-like" arrangement of the O1 and O2 atoms around the A cations effectively immobilize the large radwaste elements such as Ba, Cs and Rb. The effectiveness of these obstructions to A cation movement through the tunnels has been conclusively shown by the intensive leaching tests of Ringwood et al. (1979a). The apparent ready diffusion of the A atoms from unit cell to unit cell proposed by Beyeler (1976) and also by Dryden and Wadsley (1958) on the basis of a.c. dielectric constant measurements can be interpreted more reasonably as the movement of atoms from one equivalent 4(e) site to the other across the mirror at $(0,0,\frac{1}{2})$, within the O1 framework. This is consistent with the results of Bernasconi, Beyeler and Strassler (1979) who found the value for the d.c. conductivity of $\text{K}_{1.54}\text{Nb}_{0.77}\text{Ti}_{7.23}\text{O}_{16}$ to be negligible ($<10^{-9} (\Omega\text{cm})^{-1}$).

The magnitude of U_{33} for the A cation is very much larger than the other atoms. Little mention of this

unusually high value has been made elsewhere in the literature, although Cadée and Verschoor (1979) found a high value for the barium U_{22} in the monoclinic $Ba_{1.7}Sn_{2.6}Cr_{1.4}O_8$ hollandite phase and Fournès, Blasse and Saux (1977) also reported a large isotropic B parameter for Ti in the hollandite-type structure TiV_5S_8 . This large anisotropic thermal motion, together with the high residual at (0,0,.31) and (0,0,1) obtained from the difference fourier map indicates additional position disorder such that the refined site is the most probable over a range.

The Al, Ni and Ti atoms are co-ordinated by six oxygen atoms at the corners of distorted octahedra. These atoms are distributed randomly over special position 8(h). This site is capable of accommodating a large range of elements varying both in size and charge (for examples see Cadée and Verschoor, 1978; Bayer and Hoffman, 1966 and Ringwood et al., 1979a). These substitutions are reflected in the cell volume, being smallest for the aluminium-silicon cation combination ($V = 236.3 \text{ \AA}^3$ Reid and Ringwood, 1969) and increasing for combinations of cations with larger ionic radii e.g. titanium-gallium hollandite ($= 298.9(2) \text{ \AA}^3$ Cadée and Verschoor, 1978). To accommodate cation combinations with very large ionic radii e.g. tin and indium ($V = 353.5(2) \text{ \AA}^3$) the hollandite structure distorts slightly, lowering the symmetry to monoclinic. The volume change from the smallest to the largest hollandite compound cited above represents almost a 50% increase with the symmetry change occurring between 290 to 300 $^{\circ}\text{C}$.

Endo, Kume, Kinomura and Koizumi (1976) reported a monoclinic hollandite structure for the phase $K_2Cr_8O_{16}$. Conversion of the lattice parameters of this phase from C2/m ($a = 13.820$, $b = 2.941$, $c = 9.772$, $\beta = 135^\circ$) to I2/m results in the following cell edges of $a = c = 9.772 \text{ \AA}$ and β angle of 90° . This suggests a tetragonal hollandite structure as could be expected from the small ionic radii of Cr^{3+} and Cr^{4+} and small volume ($280.8 \text{ \AA}^3$).

Each O1 atom is co-ordinated to two A atoms and three octahedral metal atoms. The O2 atoms are co-ordinated to 3 octahedral metal atoms only.

As mentioned previously, a long exposure rotation photograph showed bands of diffuse scattering between the layer lines. This phenomenon has also been reported by various other investigators. Beyeler (1976), showed the diffuse scattering arises only from the Ba ions in the tunnels and has modelled it on the basis of cation ordering within the channels. In our present case the diffuse planes are situated at approximately 0.33 of a reciprocal lattice cell from the Bragg planes, along the c direction.

At 50% occupancy only one A site in four need be occupied, that is, one in every two unit cells (Fig. 3a). However, at higher barium concentrations adjacent cells will sometimes be occupied (Fig. 3b). Even at concentrations lower than 50% there is a probability that this will occur assuming a random growth distribution of occupied and unoccupied cells. Since the original A site on $00\frac{1}{2}$ has now been split into two sites, the problem of the close separation of A atoms in adjacent unit cells

(2.043 Å apart in the original model) can now be more readily accommodated. If an A atom resides in site R_1 (Fig. 3b), then the probability of finding an A atom at Q_1 will be zero due to size constraints. The probability of finding atoms in both Q_1 and R_2 will be negligible, again due to charge and size constraints ($Q_1 - R_2 = 2.263(4)\overset{\circ}{\text{Å}}$), and at positions R_1 and R_2 , i.e. one unit cell apart, will be the same as the original model. Occupied sites R_1 and Q_2 will be the most favoured when adjacent cells are occupied on the basis of both steric ($R_1 - Q_2 = 3.623(4)\overset{\circ}{\text{Å}}$) and electrostatic considerations. The displacements of the A ions from their idealised sites can therefore be attributed to the mutual steric and electrostatic repulsion which occurs when adjacent cells are occupied. Using the constraint that only sites whose distance is greater and equal to $R_1 - Q_2$ are occupied, then variable repeat distances are attainable i.e. the stoichiometry of the crystal varies along the channels. It is only by examining the diffuse scattering that the true ordering/disordering pattern of the A atoms will become known. Optical modelling experiments for such a purpose are currently being undertaken.

The maximum composition of the large univalent cations Rb^+ and K^+ in these channels corresponds to full occupancy (Bayer and Hoffman, 1966). Although these cations are somewhat larger than Ba^{2+} , the repulsive force has decreased thus enabling these atoms to be stable on sites at 1 unit cell distance apart. This implies a possibility that at full or near full occupancy, the univalent cations could conceivably be placed on special position 2(b) (0,0,½) as found

for $K_2Cr_8O_{16}$ (Endo et al., 1976). On the other hand, Beyeler (1976) has proposed a shift from the $(0,0,\frac{1}{2})$ position for K^+ in $K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$ hollandite, although in this structure the A site is only partially occupied. In the case of Cs^+ , Bayer and Hoffman (1966) produced only non-stoichiometric phases of $Cs_xAl_xTi_{8-x}O_{16}$. They concluded that the ionic radius of Cs^+ is too large for every unit cell to be occupied. Ringwood et al. (1979a) have shown cesium to readily replace barium in $BaAl_2Ti_6O_{16}$ hollandite forming an extensive solid solution series.

The microprobe analyses of the Ba-hollandite show the barium composition to extend over a wide range with x varying from 0.3 to 1.2, in agreement with Dryden and Wadsley (1958). This upper barium composition is also within the theoretical maximum value of x (= 1.33) using the model in Fig. 3b and assuming that during growth there was always a Ba atom available to occupy a vacant site and that only steric and charge constraints prevented it from doing so.

These formulae however, do not follow the general stoichiometry of $A_x(B_{2x}Ti_{8-2x})O_{16}$ although each individual charge gave homogeneous analyses. Furthermore, the X-ray powder photographs showed typical hollandite-type patterns. Interpretation of these analyses is made difficult by the overlap of the Ba La and Ti K α lines, resulting in large errors ($\pm$ several percent) for the weight percent of these elements. Thus, the compositions presented here should only be used as a guideline, and are not necessarily

inconsistent with hollandite stoichiometry.

Both X-ray photographs and microprobe analyses confirmed the presence of additional phases of rutile, Al_2TiO_5 and a Ba, Ti, aluminate co-existing with Ba-hollandite.

The Na analogue of this series, i.e. $\text{Na}_x(\text{Al}_y\text{Ti}_{8-y})\text{O}_{16}$, behaves differently to the other large cations, in forming the Na_xTiO_2 -type structure (Bayer and Hoffman, 1965). Although a small amount of Na has been reported to substitute in the A cation site (e.g. Norrish, 1951) the application of a large amount of pressure is needed to stabilize this cation in the hollandite-type structure (Ringwood, Reid and Wadsley, 1967).

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Table 1. Electron-microprobe analyses and calculated atomic contents.

	1*	2	3	4	5
Total	68.	81.	62.	77.	70.
Si-C ₂	7.5	11.2	13.1	13.7	12.4
FeO	<0.1				
MgO	4.7				
FeO	20.	7.	25.	9.	18.
CaO	0.2				
Al ₂ O ₃	0.5				
Total	100.7	99.2	100.1	99.7	100.4
Si ²⁺	6.40	6.75	5.91	6.45	6.48
Al ³⁺	1.10	1.46	1.96	1.8	1.42
Fe ²⁺	-				
Fe ³⁺	0.48				
Fe ²⁺	0.98	0.3	1.2	0.39	0.9
Ca ²⁺	0.03				
Al ³⁺	0.02				
Total	16.00	16.00	16.00	16.00	16.00

*Analysis of crystal used in structure determination.

Table 2. Crystal data for $(\text{Ba}_{.98}\text{Ca}_{.03}\text{Zr}_{.02})(\text{Al}_{1.18}\text{Ni}_{.46}\text{Ti}_{.44})\text{O}_{16}$

Tetragonal, $I4/m$ (C_{4h}^5 , No 87)

$$a = 10.039(1)$$

$$c = 2.943(1) \text{ \AA}$$

$$V = 296.6(1) \text{ \AA}^3$$

$$Z = 2$$

$$D_c = 4.23 \text{ g cm}^{-3}$$

$$(\text{Mo-K}\alpha) = 84.66 \text{ cm}^{-1}$$

Table 3. Final atomic co-ordinates and thermal parameters for $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ with e.s.d.'s. in parentheses.

Atom	Site	X/A	Y/B	Z/C	Beq
A	4c	0.0	0.0	0.3845(7)	2.18
B	8h	0.3512(1)	0.1673(1)	0.0	0.65
OXY(1)	8h	0.1539(3)	0.2018(3)	0.0	0.63
OXY(2)	8h	0.5410(3)	0.1658(3)	0.0	0.74

Atom	BETA11	BETA22	BETA33	BETA12	BETA13	BETA23
A	0.0029(1)	0.0029(1)	0.1225(37)	0.0	0.0	0.0
B	0.0019(1)	0.0019(1)	0.0127(4)	0.0	0.0	0.0
OXY(1)	0.0021(3)	0.0017(2)	0.0100(18)	-0.0003(3)	0.0	0.0
OXY(2)	0.0021(3)	0.0019(2)	0.0179(20)	-0.0002(3)	0.0	0.0

Atom	U11	U22	U33	U12	U13	U23
A	0.015(1)	0.015(1)	0.054(2)	0.0	0.0	0.0
B	0.010(1)	0.010(1)	0.006(1)	0.0	0.0	0.0
OXY(1)	0.011(1)	0.009(1)	0.004(1)	-0.002(2)	0.0	0.0
OXY(2)	0.011(2)	0.010(1)	0.008(1)	-0.001(2)	0.0	0.0

Table 4. Interatomic distances ($\text{\AA}$) and angles ($^\circ$) of $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ with e.s.d's. in parentheses.

A - O(1)	2.787(3)	4x	O(1) - A - O(1)	132.1(1)	
A - O(1)	3.126(3)	4x		80.51(4)	
A - O(2)	3.397(3)	4x		59.38(5)	
A - A	3.623(4)	1x		168.5(1)	
	2.943(1)	1x		103.61(2)	
	2.263(4)	1x		109.2(1)	
				70.37(4)	
B - O(2)	1.905(3)	1x	O(2) - B - O(2)	94.7(1)	O(2) - B - O(1) 173.4(1)
- O(2)	1.950(2)	2x		98.0(1)	91.5(1)
- O1	1.974(2)	2x	O(2) - B - O(1)	91.8(1)	O(1) - B - O(1) 96.4(1)
- O1	2.011(3)	1x		107.5(1)	81.9(1)
B - B	2.943(1)			82.4(1)

Fig. 1. Stereographic drawing of $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ looking down the four fold axis. A $\equiv$ Ba, Ca, Zr; B $\equiv$ Ti, Al, Ni; X $\equiv$ O(1); Z $\equiv$ O(2).

Fig. 2. Stereographic drawing of $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ with the z axis almost vertical. A, B, X, Z as for Figure 1. The program ORTEP II (Johnson, 1976) was used to provide these figures.

Fig. 3. A schematic diagram of channels showing 6 unit cells parallel to c .

• = occupied site, o = vacant site.