

**FINAL REPORT**

**Japan-Australia Co-operative Program  
on Research and Development of  
Technology for the Management of  
High Level Radioactive Wastes**

**1985 to 1998**

**Japan Atomic Energy  
Research Institute  
(JAERI)  
Tokai, Japan**

**Australian Nuclear Science  
and Technology Organisation  
(ANSTO)  
Menai, Australia**

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**Japan-Australia Co-operative Program on Research and Development of  
Technology for the Management of High Level Radioactive Wastes**

**1985 to 1998**

by

K. Hart

H. Mitamura

E. Vance

T. Banba

G. Lumpkin

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## EXECUTIVE SUMMARY

The first five-year phase (Phase I) of this Co-operative Program commenced in 1985 as a consequence of technical and diplomatic discussions in the early 1980s. During Phase I, effective mechanisms of information transfer were established through personnel exchanges between JAERI and ANSTO, and a number of technical workshops. At the end of Phase I it was agreed that the Program should be extended into a second five-year period from 1990 to 1995, designated as Phase II. This latter Phase was subsequently extended for a further three-year period from 1995 to 1998 to allow the collection of additional information on long-term accelerated damage tests and preparation of a final report. At the end of each phase of the Co-operative Program detailed results have been published in jointly-authored, formal documents. The key results, significance and recommendations of the entire Co-operative Program are summarised herein. The Co-operative Program has enhanced the excellent co-operative working relationship between the two institutions, and the arrangements developed under the original agreement should serve as a model for any other co-operative projects developed in the future.

The main activities in the first phase of the Co-operative Program were the preparation, characterisation and subsequent testing of curium-doped Synroc containing simulated waste of the type produced by the PNC reprocessing facility at Tokai in Japan namely JW-A containing elevated levels of Na. Here the leach rates increased as a consequence of the radiation damage, due to (a) microcracking at  $\alpha$ -doses corresponding to  $\geq 10^4$  years of repository storage and (b) atomic displacements within the actinide-bearing phases, zirconolite and perovskite. At high doses, corresponding to  $> 3 \times 10^4$  years of storage, the former process led to leach rate enhancements of about a factor of 10 for Na and Cs, whereas the combination of both processes led to leach rates, for Sr and Ca, that were a further order of magnitude higher. Modifications to the Synroc composition were devised to prevent microcracking when the  $\text{Na}_2\text{O}$  content of the Synroc exceeds  $\sim 1.5$  wt%.

In the second phase of the Co-operative Program, comparative studies were carried out on Synroc containing Na-free PW-4b waste and in this case, after  $\sim 10^5$  years of equivalent storage, Sr and Ca leach rates increased by a factor of 10, whereas the leach rate of Ba which is not contained in the actinide host phases did not increase with equivalent storage time. The density decrease due to radiation damage was less in samples stored at  $200^\circ\text{C}$  than at  $30^\circ\text{C}$ . Complementary studies on Cm-doped single-phase zirconolite and perovskite were carried out and studies on naturally-occurring zirconolites were initiated to provide insight into the long-term durability of zirconolite over geological time.

In both phases of the Co-operative Program, the preparation of the Cm-doped samples was carried out in JAERI's WASTEF facility at Tokai, with technical input and assistance provided by ANSTO where necessary. The results, described in greater detail in this report have confirmed the potential of Synroc as a second-generation waste form.

## 要 約

1980年代初めに行われた技術的及び外交的な話し合いの結果、本研究協力計画は最初5カ年計画（第一フェーズ）として1985年に始められた。第一フェーズでは、原研とANSTO間の人員の相互派遣及び技術的な討論のためのワークショップの開催を通じて、効率的な情報交換の成果をあげることができた。これらの成果を受け、当初の目的を達した第一フェーズに引き続き、1990年から更なる5カ年計画（第二フェーズ）が始められた。この第二フェーズは、放射線損傷に関する補完的な $\alpha$ 加速試験を行い、研究協力計画最終報告書を作成するため、1995年からさらに3年間延長された。研究協力計画における詳細な結果は、各フェーズ終了ごとに両研究所共著の正式な報告書として公表してきた。そこで、この最終報告書では研究協力計画全体を通じた主要な結果や意義及び提言についてまとめた。本研究協力計画は両研究所間のすばらしい協力関係を確立すると共に、親協定の下で進められた本計画が、将来実施される他の協力計画の良いモデルになるものと期待される。

第一フェーズの主な活動は、シンロックの耐放射線性に関する試験であり、その内容は日本の動力炉核燃料開発事業団の再処理工場から発生する高濃度のナトリウムを含む高レベル廃棄物を模擬したJW-A廃棄物にキュリウムを添加したシンロックの作製と $\alpha$ 加速試験及び特性試験である。加速年数1万年以上での微小亀裂の発生及びアクチノイド母相（ジルコノライトやペロプスカイト）における原子はじき出しによる放射線損傷の結果、浸出率の増加が観察された。加速年数3万年以上では、微小亀裂の発生により、ナトリウム及びセシウムの浸出率が約10倍高くなり、これに原子はじき出しによる放射線損傷の影響が加わって、ストロンチウムとカルシウムの浸出率はさらに10倍高くなった。このため、シンロック内のナトリウム含有率が1.5%を越える場合には、微小亀裂の発生を抑えるためにシンロック組成の改良を提案した。

第二フェーズでは、ナトリウムを含まないPW-4b廃棄物を固化したシンロックについて同様の試験を実施した。この場合は、加速年数10万年後にストロンチウムとカルシウムの浸出率は10倍大きくなったが、非アクチノイド母相に含まれるバリウムの浸出率には増加が見られなかった。一方、200℃で保持された場合の放射線損傷による密度減少は、室温保時の場合より顕著に小さくなった。さらに、キュリウムを添加したジルコノライト及びペロプスカイトに関して補完的な研究を行うと共に、地質年代にわたる長期間の安定性を確認するため天然のジルコノライトに関する研究を行った。

本研究協力計画の両フェーズにおいて、キュリウム添加試料は原研WASTEFで作製され、これに必要な技術的情報の提供や支援がANSTOによって成された。この最終報告書に詳しく述べられている様に、得られた結果はシンロックが第二世代の廃棄物固化体として有望であることを確信させるものであった。

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## **1. INTRODUCTION**

### **1.1 Historical Outline**

The current strategy for the treatment and disposal of the high-level wastes (HLW) resulting from the reprocessing of spent nuclear power reactor fuel is to solidify them into a stable form, store for an adequate term, and eventually to dispose of the solidified waste in an underground repository. In Japan, as in several other countries, the preferred solidification technology is vitrification. However, ceramics can also be used to solidify HLW, as demonstrated by the work of the Pennsylvania State University group in the mid-1970s. Then in 1978 Professor A. E. Ringwood of the Australian National University (ANU) developed and patented 'Synroc' a titanate-based ceramic waste form. Synroc consists of a thermodynamically-compatible assemblage of titanate minerals that have the capacity to accept into their crystal structures the majority of the elements present in HLW. Moreover, the naturally-occurring counterparts of these Synroc minerals have survived over geological time. In 1979, the Australian Atomic Energy Commission (AAEC), now the Australian Nuclear Science and Technology Organisation (ANSTO), joined with the ANU to participate in the development of the Synroc concept and in 1982 the Australian Government funded the AAEC to design and construct a non-radioactive full-scale Synroc demonstration plant, and supported laboratory-scale facilities for fabrication and testing of Synroc containing certain radionuclides.

During the early 1980s technical and diplomatic discussions were in progress between Australia and Japan with a view to establishing formal collaboration in research and development on the technology for the management of HLW. These discussions culminated in the exchange of Notes Verbales between the Governments of Japan and Australia on 2nd May 1984. This established a Co-operative Program under the aegis of the Science and Technology Agency (STA) of Japan and the Department of Resources and Energy (DRE) [later replaced by the Department of Primary Industries and Energy (DPIE)] of Australia. The Japan Atomic Energy Research Institute (JAERI) and the AAEC were designated as lead institutions in implementing the Co-operative Program. These two organisations formalised this arrangement through a Memorandum of Understanding signed on 3rd May 1984 and an Implementing Arrangement signed on 3rd September 1985 in Tokyo.

The purpose of the Co-operative Program was to promote the exchange of information between the designated institutions in Japan and Australia on the technology for the management of HLW and to encourage collaboration between these institutions in research and development relevant to such technology. Initially, the main focus of the Program was to evaluate the Synroc system for the management of HLW<sup>1</sup>.

In 1989 it was agreed that the Program should proceed into Phase II, a second five-year program to be carried out between 1990 and 1995. This phase was then extended for a further three years to 1998.

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<sup>1</sup> At a later date (1986) the scope of the Co-operative Program was widened to include JAERI participation in the Alligator Rivers Analogue Project (ARAP) being conducted by the AAEC.

The responsibilities of JAERI and ANSTO (and the AAEC) in each phase of work under the Co-operative Program are listed in **Appendix 1**.

## **1.2 Program Management and Formal Structure**

The overall management of the Program was assigned to a Co-ordinating Committee which consisted of representatives of the respective Government Departments - the Science and Technology Agency (STA) from Japan and the Department of Primary Industries and Energy (DPIE)] from Australia - and the designated institutions — JAERI, in collaboration with the Power Reactor and Nuclear Fuel Corporation - PNC and ANSTO, in partnership with the Australian National University (ANU). The Co-ordinating Committee has met eleven times at approximately 18 month intervals, with meetings alternating between Japan and Australia and with a Chairman provided by the Government Department of the host country. Details of these meetings are given in **Appendix 2** of this report.

In addition to the Co-ordinating Committee, the Implementing Arrangement provided for the establishment of a Steering Committee to review the technical progress of the Co-operative Program and to discuss future plans, including personnel exchanges. The Steering Committee meets at least once a year in either Japan or Australia with the chairman provided by the host institution, and receives reports on technical progress from the lead institutions. The Steering Committee reports to the Co-ordinating Committee. There have been a total of 25 meetings held (see **Appendix 2** for details of these meetings).

## **1.3 Program Objectives**

The responsibilities of the two co-operating organisations for 1985-90, 1990-95 and 1995-98 were laid down in the agreements covering each phase of the work. In broad terms the objectives of the program were to collaborate on Synroc research and development with an emphasis on complementary results from each organisation's work and on maximising exchange of information, results and personnel. The tasks carried out by the two lead organisations between 1985 and 1998 are given in **Appendix 1**.

## **1.4 Personnel Exchange**

There have been reciprocal visits of staff attending meetings of the Co-ordinating and Steering Committees and 19 longer-term exchanges of staff (see **Appendix 3** for details).

## **1.5 Workshops**

Six workshops have been held under the Co-operative Program. These workshops have allowed the dissemination of research results, encouraged technical information exchange and permitted detailed technical discussion of topics of current interest. Details of these workshops are given in **Appendix 4**.

## 2. ACTINIDE-DOPED REFERENCE SYNROC ACCOMMODATING SIMULATED PW-4B WASTE

### 2.1 Background

Incorporation of actinides in Synroc containing simulated PW-4b waste was investigated in the mid 1980s by both organisations. At ANSTO, samples containing low levels of Np (0.13 and 1.3 wt%  $^{237}\text{Np}$ ), Am (0.0005 and 0.005 wt%  $^{241}\text{Am}$ ), Pu (0.043, 0.43 and 0.62 wt%)<sup>1</sup> and  $^{244}\text{Cm}$  (0.00004 and 0.0004 wt %) were fabricated to investigate the aqueous leaching behaviour of these elements. In a complementary study at JAERI, comparable samples of Synroc were made with ~ 1 wt% of  $^{244}\text{Cm}$  to study accelerated  $\alpha$ -decay damage analogous to that experienced by waste forms over geological time scales.

### 2.2 Fabrication of Actinide-Doped, Reference Synroc

The nominal composition of the Cm-doped, simulated PW-4b waste is shown in Table 2.2.1.

**TABLE 2.2.1**  
**Composition of Cm-doped, Simulated PW-4b HLW**

Element	Content (wt%)	Element	Content (wt%)
SrO	2.52	Cs <sub>2</sub> O	8.42
Y <sub>2</sub> O <sub>3</sub>	1.44	BaO	3.82
ZrO <sub>2</sub>	11.43	CeO <sub>2</sub>	11.43
MoO <sub>3</sub>	11.96	Nd <sub>2</sub> O <sub>3</sub>	6.90
RuO <sub>2</sub>	7.26	CmO <sub>2</sub> +PuO <sub>2</sub>	21.50
Rh <sub>2</sub> O <sub>3</sub>	1.38	Fe <sub>2</sub> O <sub>3</sub>	3.70
PdO	3.48	Cr <sub>2</sub> O <sub>3</sub>	0.84
Ag <sub>2</sub> O	0.19	NiO	0.34
CdO	0.29	P <sub>2</sub> O <sub>5</sub>	1.64
TeO <sub>2</sub>	1.42		
		Total	100.0

Detailed information on the samples containing 0.91 wt% of  $^{244}\text{Cm}$  prepared in the JAERI hot-cell facilities is given in Mitamura *et al.* [1994] and Banba and Hart [1996]. The specialised techniques and equipment used in preparation of these samples is documented by Amaya *et al.* [1986], Mitamura *et al.* [1986] and Mitamura [1997].

<sup>1</sup> The Pu used in these experiments was not pure  $^{239}\text{Pu}$  but also contained  $^{240}\text{Pu}$  (half-life = 6500 years) and  $^{241}\text{Pu}$  (half-life = 13 years). Furthermore,  $^{241}\text{Am}$  had ingrown from  $^{241}\text{Pu}$ . As  $^{241}\text{Pu}$  is a  $\beta$ -emitter and the  $\alpha$ -energies of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  overlap, it is not possible to distinguish between them by  $\alpha$ -spectrometry; consequently, the reported Pu leach rate is based on  $^{239}\text{Pu} + ^{240}\text{Pu}$ .

The samples prepared using the JAERI hot cell facilities contained 10.90, 87.12 and 1.98 wt% of simulated PW-4b waste, precursor material and titanium metal, respectively. The respective specific  $^{244}\text{Cm}$  and total  $\alpha$ -activities of the samples were 27.4 (0.741) and 27.5  $\text{GBq g}^{-1}$  ( $0.744 \text{ Ci g}^{-1}$ ) on February 28, 1990.

### **2.3 Characterisation of Actinide-Doped, Reference Synroc**

**Microscopy Studies** — Blackford *et al.* [1992] carried out an AEM study on a suite of actinide doped Synroc specimens prepared by ANSTO [Reeve *et al.*, 1989]. Their results confirmed the three-phase mineralogy and showed that Pu and Np were preferentially incorporated in zirconolite by factors of 5 and 10, relative to perovskite on a wt% basis. No partitioning of actinides into hollandite was observed. Furthermore the microstructures and phase distributions observed in these actinide-doped Synroc samples were similar to those seen in specimens containing simulated HLW fabricated in the open laboratory.

**XRD** — X-ray diffraction studies were undertaken at JAERI on the Cm-doped, Synroc samples prepared in their hot cell facilities. **Figure 2.3.1** shows XRD patterns from a Cm-doped sample that had accumulated a dose of  $12.4 \times 10^{17} \alpha\text{-decays.g}^{-1}$  (equivalent age, 16,000 yr), before and after annealing at  $800^\circ\text{C}$  for 12 h in a graphite crucible. After the heat-treatment, it was assumed that all the radiation damage had been annealed and that the sample was in the as-fabricated state. The X-ray patterns measured after annealing confirmed that the specimen consisted of the usual, hollandite, perovskite, and zirconolite, plus a minor phase assumed to be hibonite (see **Section 3.2**). Peak intensities of zirconolite and perovskite, relative to that of the (130)/(310) hollandite peak are less in the as-damaged condition than in the annealed state. This result confirms that the short-range, actinide recoil nuclei cause atomic disorder in their host-phases and consequently hollandite is less affected by  $\alpha$ -decay damage.

### **2.4 Physical Properties of Actinide-Doped, Reference Synroc**

The densities of two cylinders, 2-cm-diameter x 1-cm-high, (designated as S90002 and S90005) were periodically measured by the water displacement method. Two samples were cut from another cylinder and annealed at  $1000^\circ\text{C}$  for 2 h in a graphite crucible. After heat treatment, one sample (R1-5) was stored at  $200^\circ\text{C}$ , and the other (R1-6) was stored at room temperature. Densities of these samples were measured periodically in the same manner as above. The effect of  $\alpha$ -decay damage on density for samples S90002 and S90005 is shown in **Figure 2.4.1**. The change in density with increasing  $\alpha$ -dose was essentially constant, suggesting that, thus far, no macrocracking due to volume expansion had occurred. **Figure 2.4.2** shows that storage of the sample at  $200^\circ\text{C}$  reduced the volume expansion per unit  $\alpha$ -dose by a factor of 2 compared to that of the sample stored at room temperature.

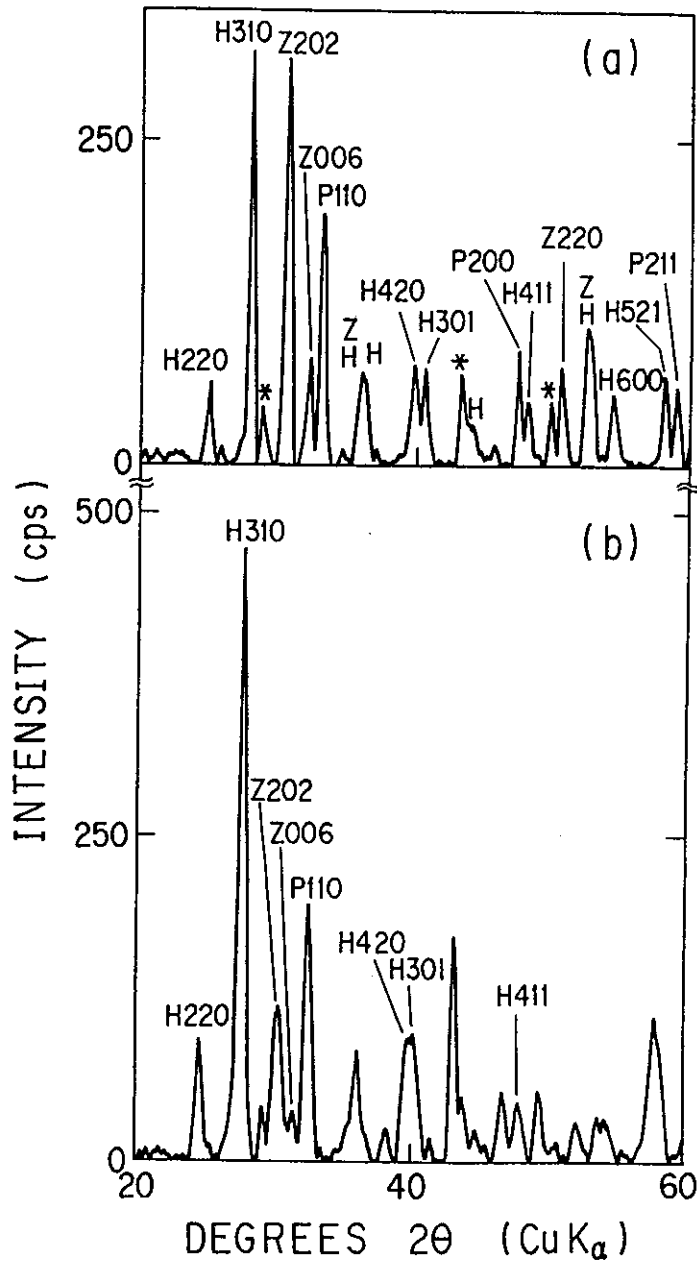


Figure 2.3.1 X-ray diffraction patterns from (a) annealed and (b) as-damaged Cm-doped, reference Synroc containing simulated PW-4b waste. The sample was subjected to a dose of  $12.4 \times 10^{17}$   $\alpha$ -decays  $g^{-1}$ , and then annealed at 800°C for 12 h.

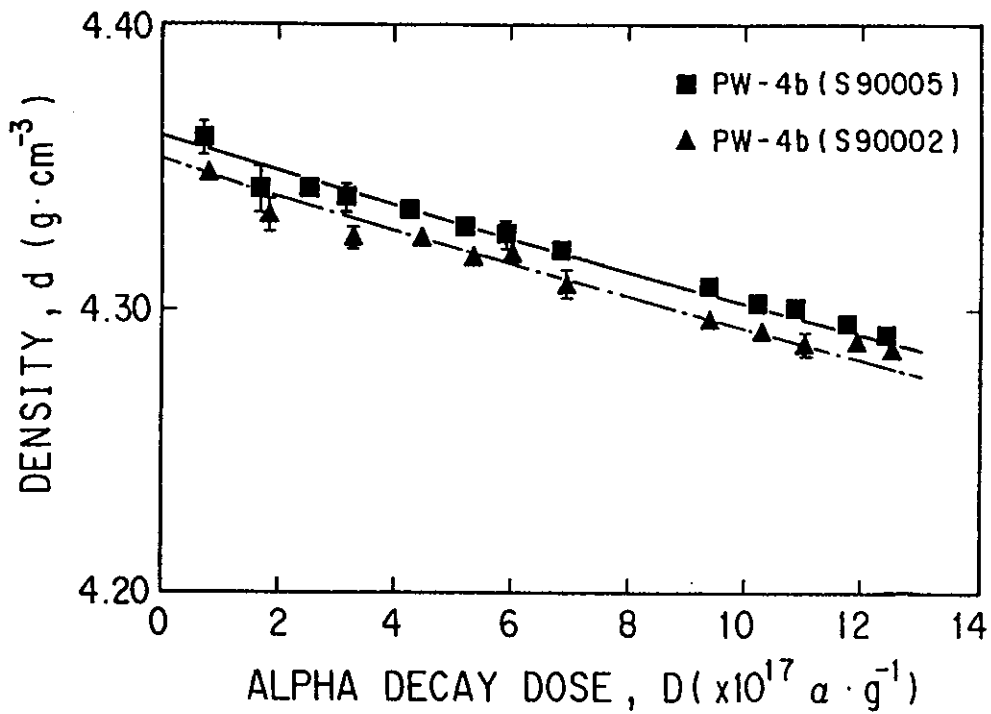


Figure 2.4.1 Change in density for two samples of Cm-doped Synroc, containing simulated PW-4b waste, versus  $\alpha$ -decay dose. Samples S90002 and S90005 were hot-pressed at 1200°C/29 MPa for 1 h and 2 h.

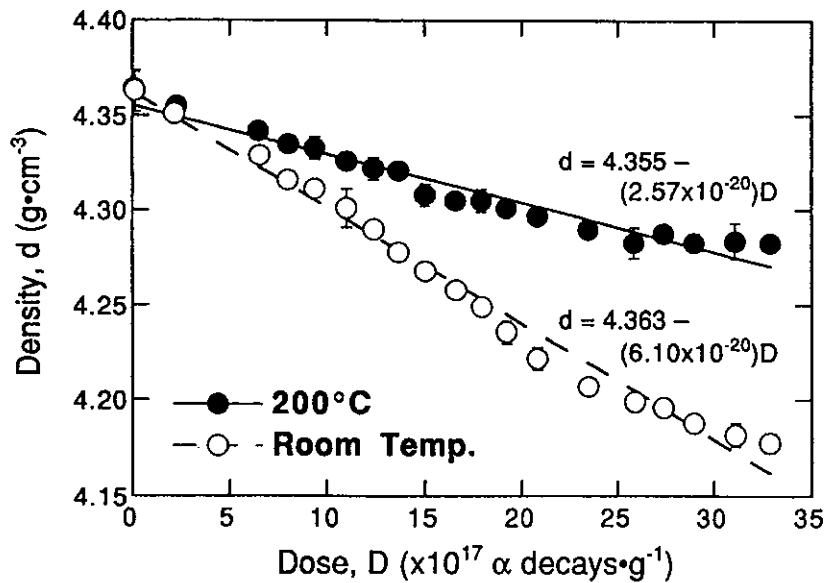


Figure 2.4.2 Effect of storage temperature on the relationship between density and  $\alpha$ -dose.

## 2.5 Leaching Behaviour of Actinides Released from Reference Synroc

### 2.5.1 Studies at ANSTO of actinide-doped Synroc

Figure 2.5.1 compares the normalised solution leach rates of Np, Pu, Am and Cm in deionised water at 70°C measured at ANSTO. The leachability of the actinide elements decreased in the order: Np > Am > Pu > Cm. Typically, most of the Np is in solution (83%), in contrast to the other actinides where most of the activity released into solution was associated with the vessel walls. Moreover, the leach rates of the actinides decreased with time and the overall results confirmed that, as a group, these elements are the least leachable of all the HLW elements.

These results, which suggest that Np release is not associated with incorporation of this actinide into secondary or surface phases, are consistent with the microscopy results [Smith *et al.*, 1995] that showed no surface enrichment of Np (at levels > 0.1 wt%, i.e. the detection limit of EDS).

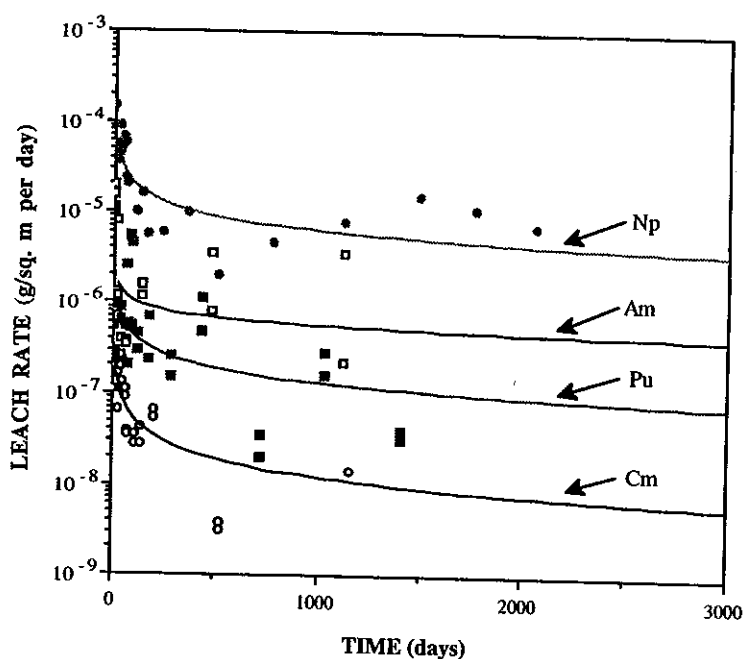


Figure 2.5.1 Leach rates of Np, Pu, Am and Cm, based on solution analyses, measured in deionised water at 70°C.

#### 2.5.1.1 Leaching under anoxic conditions

Studies under anoxic conditions have been carried out, at ANSTO, in a glove box with a nitrogen atmosphere containing less than 20 ppm O<sub>2</sub>. All filtration procedures were completed within the glove box and the filtrates were acidified before they were removed.

**Np-doped Synroc** —Blackford *et al.*'s [1992] study confirmed the suppression of Np release by anoxic leaching conditions and was further supplemented with anoxic conditions in the presence of geological materials (see below). Studies in deionised water showed that:

- Solution leach rates under oxic conditions were similar to those measured under anoxic conditions. However, under oxic conditions most of the leached Np (83%) was in ionic form, while under anoxic conditions, filtration reduced the activity of Np by a factor of 24, suggesting that the Np was predominantly in the form of fine particulates.
- The measured concentrations of Np in solution are lower than predicted solubility limits, suggesting that matrix effects rather than the intrinsic solubility of Np control the release from Synroc under both oxic or anoxic conditions.

**Interaction with geological materials** — Leaching of Np-doped Synroc in the presence of Mol Boom clay under an anoxic atmosphere [Hart *et al.*, 1994] has established that;

- Under anoxic conditions the differential leach rate of Np is low ( $5 \times 10^{-5} \text{ g m}^{-2} \text{ d}^{-1}$ ) and not enhanced by the presence of Boom clay.
- The presence of Boom clay did not markedly affect the distribution of Np between aqueous solution species and filterable colloidal components.

Under anoxic conditions, the smaller soluble Np fraction measured in deionised water compared to clay-buffered leachates, probably reflects formation of very insoluble species, such as Np-oxides. This illustrates a caveat for 'standard' leach-test procedures emphasising that leach rates and radionuclide solubilities should be measured under geologically relevant conditions if the results are to be used for performance assessment purposes.

### 2.5.2 Studies at JAERI of Cm-Doped Synroc

Half-disc specimens of Cm-doped Synroc have been leach tested in triplicate using the MCC-1 test method at 90°C for 56 days, using four, seven-day leach periods followed by a 28 day period. After pH measurement and addition of 0.1 cm<sup>3</sup> concentrated nitric acid, leachate samples were withdrawn from the glove box and subjected to NaI (TI)  $\gamma$ -ray spectrometry and liquid analyses using ICP/AES (Ca, Mo and Ba) and AAS (Cs and Sr).

Cm-doped Synroc samples containing simulated PW-4b waste which had accumulated different levels of  $\alpha$ -decay damage corresponding to equivalent ages of (a) 50, (b) 13,000, (c) 30,000 and (d) 113,000 years were leach tested as above. **Figures 2.5.2 and 2.5.3** show the change in average leachate pH and Eh as a function of leaching time. Generally, the pH of specimen-charged leachates is lower than that of the blank leachate although for the more damaged specimens the scatter among the three data sets are larger. The large scattering in pH implies some deterioration of the chemical durability due to  $\alpha$ -damage. For all leach tests, the average Eh of the specimen-charged leachate is similar to that of the blank leachate, with the exception of the final leaching period where for the more damaged specimens the Eh of the specimen-charged leachate is lower.

**Figure 2.5.4** summarises the leach rates of inactive elements with time. In all cases, the leach rates decrease quickly with time. The leach rates of inactive elements diminish in the following order:



The leaching behaviour of Cs is complicated. For specimens with an equivalent age of 50 years, the leach rates of Cs and Ba are similar but for more damaged specimens the Cs leach rate is a factor of between 2 and 29 higher than that of the 50 year sample (see Figure 2.5.4). The increase in Ca and Sr leach rates is less marked and Mo and Ba leach rates do not vary significantly with increasing  $\alpha$ -damage. The increase in Ca and Sr leach rates occurs with increasing  $\alpha$ -decay damage to the perovskite phase. However, Cs and Ba are both incorporated in the hollandite phase, which does not incorporate actinide elements. Therefore, it is possible that the enhanced release of Cs over Ba from the more damaged specimens may be due to the exposure of fresh intergranular phases rich in Cs.

Figure 2.5.5 shows the effect of time on the average total leach rates of  $^{244}\text{Cm}$  for the specimens with equivalent ages of 50, 430, 13,000, 30,000 and 113,000 years. The leach rates do not change significantly with increasing  $\alpha$ -damage, and are instead apparently controlled more strongly by the pH of the leachant.

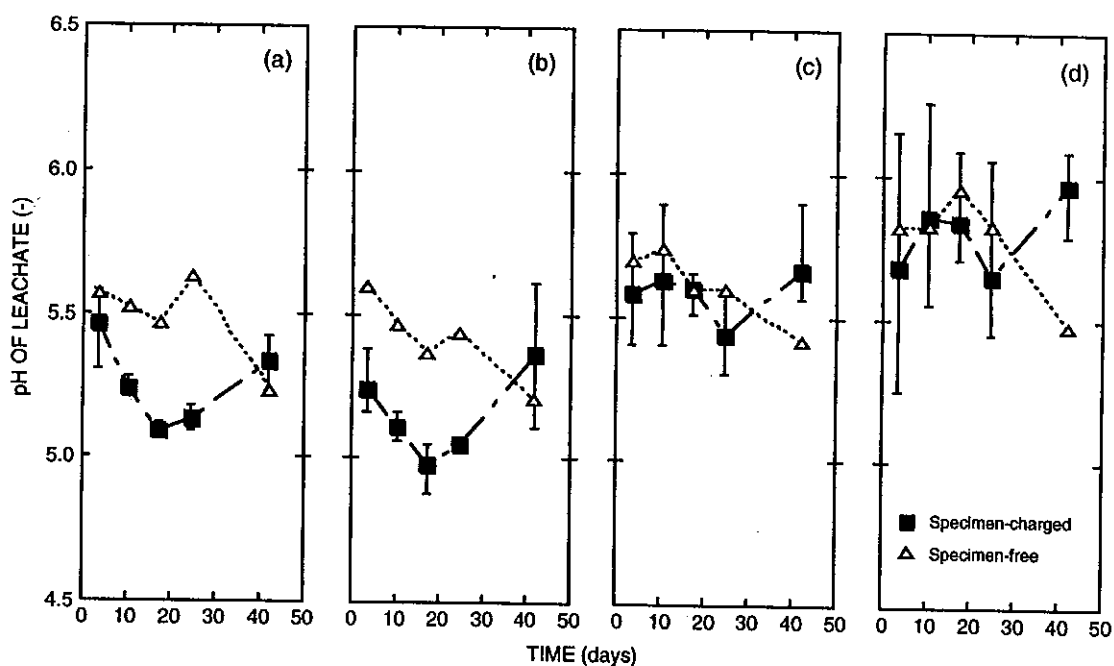


Figure 2.5.2 Change in pH of leachate from Cm-doped, reference Synroc containing Cm-doped PW-4b waste of different storage ages — (a) 50 years: (b) 13,000 years: (c) 30,000 years and (d) 113,000 years.

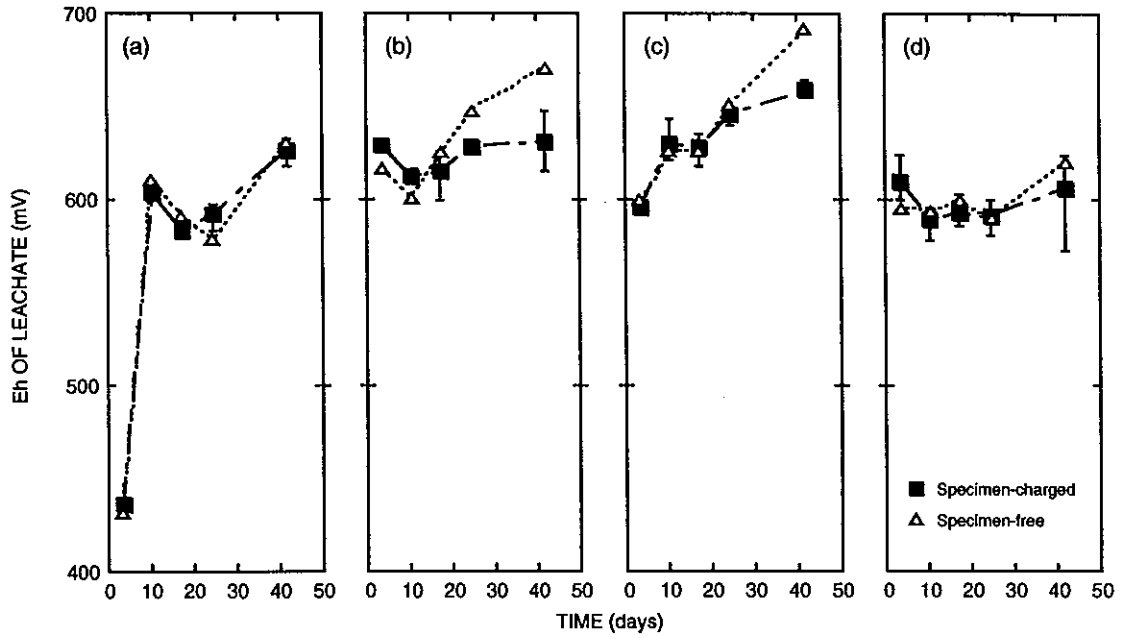


Figure 2.5.3 Change in Eh of leachate from Cm-doped, reference Synroc containing Cm-doped PW-4b waste of different storage ages — (a) 50 years: (b) 13,000 years: (c) 30,000 years and (d) 113,000 years.

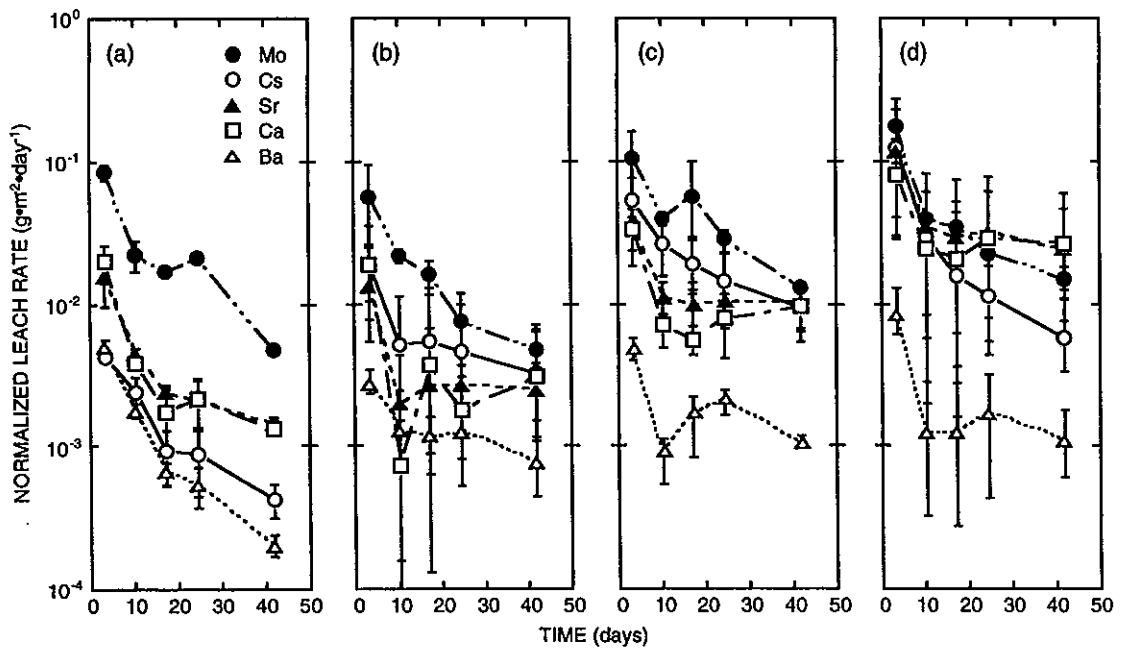


Figure 2.5.4 Comparison of normalised leach rates of indicator elements from reference Synroc containing Cm-doped PW-4b waste of different storage ages — (a) 50 years: (b) 13,000 years: (c) 30,000 years and (d) 113,000 years.

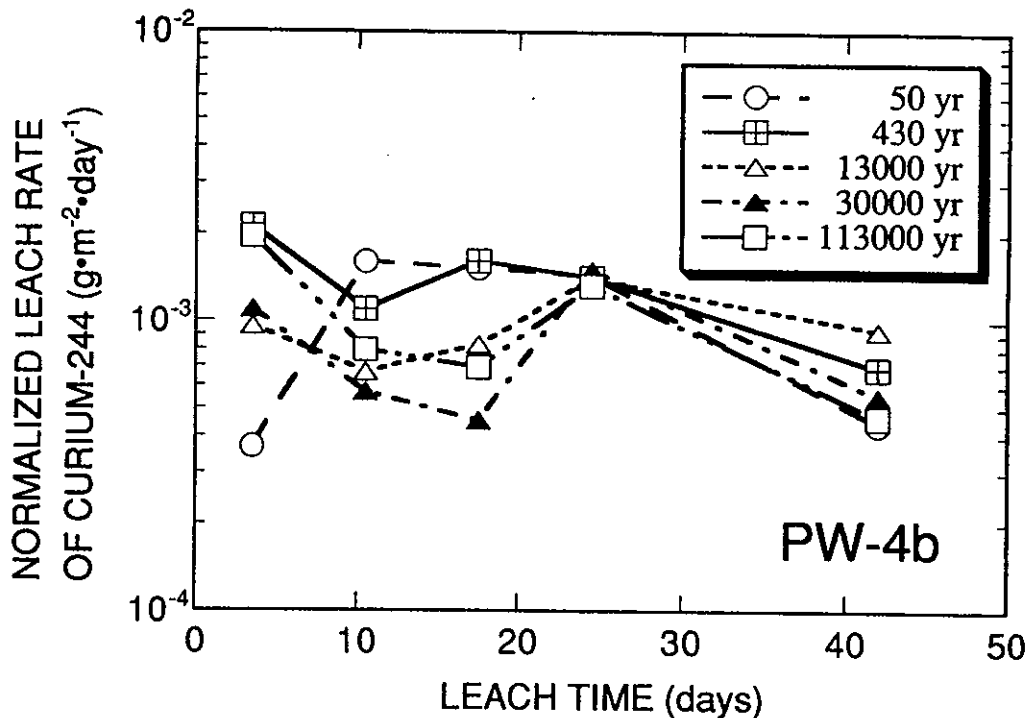


Figure 2.5.5 Comparison of normalised leach rates of  $^{244}\text{Cm}$  from reference Synroc containing simulated PW-4b waste of different equivalent storage ages.

## 2.6 Effect of the Level of Cm-doping on Leach Rates from Synroc

ANSTO experiments with Synroc samples doped with 0.0004 wt% of Cm yielded long-term leach rates of  $\sim 10^{-5} \text{ g m}^{-2} \text{ d}^{-1}$  [Hart *et al.*, 1991]. In studies of Cm-doped Synroc containing  $\sim 1$  wt% of Cm [Mitamura *et al.*, 1994], the normalised, total leach rate of Cm approached  $\sim 10^{-3} \text{ g m}^{-2} \text{ d}^{-1}$  at  $90^\circ\text{C}$  after 56 days, i.e. a factor of  $\sim 100$  greater. This occurred even though leach rates of other, inactive elements were comparable for both samples. It was not possible to establish whether this enhanced leach rate was attributable to accelerated radiation damage alone. There is a possibility that other factors were involved. Specifically, the interaction of  $\alpha$ -activity with the Teflon leach vessels was a concern because HF would then be released thereby establishing an acid environment which in turn leads to enhanced leach rates. In order to resolve the above issue, a suite of samples doped with 0.04, 0.004 and 0.0004 wt%  $^{244}\text{Cm}$  was prepared at ANSTO. The batch containing 0.04 wt% Cm was leached in the Teflon vessels from JAERI and, for reference in the polyethylene containers routinely used at ANSTO.

Leaching was carried out in deionised water at  $70^\circ\text{C}$  on triplicate samples. The results from the leaching tests show that there is no effect of curium-doping, at 0.0004 to 0.04 wt% levels, on the leach rates of curium from Synroc, and, moreover that Teflon-induced acidification is insignificant at doping levels below 0.1 wt% Cm [Hart *et al.*, 1997].

### **3. MODIFICATION OF REFERENCE SYNROC TO ACCOMMODATE SIMULATED JW WASTE**

#### **3.1 Background**

In the early work on Synroc carried out in Australia, the composition of the waste simulant was equated with the US reference PW-4b formulation. The development of the Synroc precursor material at the AAEC and ANU was therefore designed to accommodate PW-4b waste, with waste loadings to ~ 30%. In Japan, reprocessing involves the addition of sodium as Na<sub>2</sub>CO<sub>3</sub> for reconditioning of TBP damaged by irradiation. This results in a waste stream that contains between 16 and 19 wt% Na<sub>2</sub>O. Compositions of reference JAERI (JW-A and the closely related JW-A 'modified') are given in **Table 3.1.1** and a variant of JW-A in which potassium replaces sodium. The US PW-4b waste composition is also tabulated for reference.

Sodium in the JW-A waste does not readily enter into hollandite and zirconolite. The inventory of sodium (and iron) in JWA-A waste is substantial — more than enough to saturate the hollandite, zirconolite and perovskite phases of Synroc, at 10 to 20 wt% loadings. As a result, new and additional phases appear, namely the Na-rich phases freudenbergite (Na<sub>2</sub>(Al,Fe)<sub>2</sub>Ti<sub>6</sub>O<sub>16</sub>) and loveringite (Ca(Ti,Fe,Mn)<sub>21</sub>O<sub>38</sub>). As long as these phases are encapsulated by the more durable phases of the reference Synroc, the leaching performance of fully dense Synroc will not be adversely affected. However, as the waste loading, and hence the amount of supplementary minerals increases, the likelihood of total encapsulation decreases.

As a consequence of discussions held at one of the early Steering Committee Meetings (Meeting No. 5, September 1987), a systematic study of Cs leach rates of Synroc containing various loadings of modified JW-A waste was carried out at ANSTO in close collaboration with JAERI. The results of these investigations, summarised in **Table 3.3.1**, showed that for waste loadings of up to 14% (corresponding to 2.6 wt% of Na<sub>2</sub>O) the Cs leach rate of Synroc did not increase significantly. However at higher waste loadings, the Cs leach rate increased by up to three orders of magnitude. Consequently, it was decided that for the accelerated radiation damage experiments using Cm-doped Synroc the Na<sub>2</sub>O content would be restricted to 1.65 wt% — the equivalent to a 10% loading of JW-A waste.

**TABLE 3.1.1**  
**Composition of Simulated High Level Wastes (wt%)**

WASTE	Composition (wt%)			
	JW-A	JW-(Mod)	PW-4b	JW-K
<b>Fission Products</b>				
SeO <sub>2</sub>	0.11	0.09	0.20	0.08
Rb <sub>2</sub> O	0.63	0.52	0.96	0.46
SrO	1.76	1.44	2.66	1.27
Y <sub>2</sub> O <sub>3</sub>	1.04	0.85	1.50	0.75
ZrO <sub>2</sub>	8.53	9.91	12.07	8.71
MoO <sub>3</sub>	9.00	7.39	12.55	6.50
MnO <sub>2</sub>	1.34	1.10	-	0.97
TcO <sub>2</sub>	-	-	2.59	-
RuO <sub>2</sub>	5.06	4.16	7.60	3.66
Rh <sub>2</sub> O <sub>3</sub>	1.05	0.86	1.43	0.76
PdO	2.77	2.28	3.60	2.00
Ag <sub>2</sub> O	0.15	0.12	0.20	0.11
CdO	0.16	0.13	0.30	0.12
SnO <sub>2</sub>	0.10	0.08	0.28	0.07
Sb <sub>2</sub> O <sub>3</sub>	0.03	0.03	0.09	0.03
TeO <sub>2</sub>	1.18	0.97	1.49	0.85
Cs <sub>2</sub> O	5.07	4.17	7.42	3.66
BaO	3.24	2.67	3.98	2.35
La <sub>2</sub> O <sub>3</sub>	2.63	2.16	3.63	1.90
CeO <sub>2</sub>	7.03	6.74	8.09	5.91
Pr <sub>6</sub> O <sub>11</sub>	2.57	2.11	3.42	1.85
Nd <sub>2</sub> O <sub>3</sub>	8.56	7.03	11.24	6.17
Sm <sub>2</sub> O <sub>3</sub>	1.70	1.39	2.20	1.22
Eu <sub>2</sub> O <sub>3</sub>	0.32	0.26	0.46	0.23
Gd <sub>2</sub> O <sub>3</sub>	0.20	0.16	0.25	0.14
U <sub>3</sub> O <sub>8</sub>	-	-	4.64	-
<b>Process Chemicals</b>				
Na <sub>2</sub> O	16.52	18.88		
K <sub>2</sub> O	-	-	-	28.70
P <sub>2</sub> O <sub>5</sub>	1.67	1.29	1.71	1.13
Al <sub>2</sub> O <sub>3</sub>		6.88		6.05
<b>Corrosion Products</b>				
Fe <sub>2</sub> O <sub>3</sub>	13.83	12.46	3.84	10.95
Cr <sub>2</sub> O <sub>3</sub>	2.01	2.15	0.88	1.89
NiO	1.74	1.72	0.36	1.51

### 3.2 Formulation of New Precursor for JAERI Waste

Incorporation of a few wt% Na<sub>2</sub>O into the normal Synroc-C formulation leads to the formation of new Na-rich phases [Buykx *et al.*, 1988]. The most abundant and commonly observed "extra" phase in Synroc containing JW-A waste is freudenbergite. Other minor phases that may be stabilised are loweringite and hibonite, CaAl<sub>12</sub>O<sub>19</sub>. Kesson and Ringwood [1981] have shown that sodium could be accommodated in the perovskite phase in Synroc provided that rare earths were present as trivalent charge compensators but this strategy may not be optimum. At ANSTO a preparation consisting of 20% rare earths plus 80% (oxide equivalent) of the reference Synroc precursor was combined with 20% JW-A waste. The final waste loading was 17% and sufficient rare earths were present to allow Na<sup>+</sup> to be accommodated in perovskite as an Na<sub>0.5</sub>RE<sub>0.5</sub>O<sub>3</sub> component. Detailed examination by electron microscopy and X-ray diffraction on a sample hot pressed at 1200°C confirmed that the desired three-phase mineralogy had been achieved, but the Cs leach rate was 12 times that of the sodium-free reference Synroc.

From the perspective of fabrication, the main difference between Synroc containing JW-A waste and standard Synroc is that the sodic variant exhibits a lower melting temperature (by up to 90°C [Cassidy and Stewart, 1990] and its consolidation during hot-pressing is beneficially enhanced [Stewart and Buykx, 1990].

An alternative conceptual approach involves substituting the corresponding potassium compound for its sodium counterpart in the waste reprocessing sequence. The composition of a potassium variant of modified JW-A waste is shown in Table 3.1.1 [Vance *et al.*, 1991]. Unlike sodium, potassium can be readily incorporated into the hollandite structure at normal waste loadings and no new phases appear in the mineralogy.

### 3.3 Leaching Behaviour of Non-Radioactive JW-Synroc

Table 3.3.1 compares the 7 day leach rates of Synroc incorporating sodium containing JW-A waste, modified JW-A waste plus an additional 17 wt% of rare earth oxides (JW + REO), the variant of JW-A in which sodium is replaced by potassium (JW-K), and reference Synroc containing simulated PW-4b waste.

The chemical durability of specimens containing JW-A and PW-4b waste at loadings of 10 and 14 wt% is good (see Table 3.3.1). However at a waste loading of 20 wt% (3.8 wt% Na<sub>2</sub>O) and above there is a marked deterioration in the leaching performance. Samples containing 28% modified JW-A waste had very high Cs, Al, Mo and Na leach rates. Moreover after leaching, the solutions had higher pHs, 10 to 11, than those with waste loadings < 14 %, typically pHs of 7 to 8. There is a strong correlation between Na content and leachability of the more mobile fission products, Cs and Mo.

TABLE 3.3.1  
Effect of Waste Formulation on Synroc Leach Rates

Type of Waste	Loading (wt%)	Na <sub>2</sub> O (wt%)	Leach Rates <sup>§</sup> (g m <sup>-2</sup> d <sup>-1</sup> )				
			Ba	Ca	Cs	Mo	Sr
PW-4b	10	nil	0.09	0.023	0.08	0.3	0.026
	20	nil	0.10	0.04	0.20	0.9	0.2
	30	nil	0.20	0.06	0.10	1.0	0.2
	35	nil	1.0	0.2	0.10	2.0	1.0
	40	nil	0.1	0.7	300.0	10.0	2.0
JW-A	10	1.9	0.005	0.01	0.18	0.1	<0.002
	14	2.6	0.014	0.004	0.16	0.16	<0.002
	20	3.8	<0.0004	<0.0001	4.9	1.2	<0.002
	28	5.3	<0.0004	<0.0001	93.0	12.1	<0.002
JW(+REO)	17	3.2	0.03	0.03	1.0	<0.05	0.03
JW-K	10	nil	0.03	0.01	<0.01	0.2	0.01
	20	nil	0.13	0.015	0.4	0.6	0.02
	30	nil	0.015	0.02	0.5	<0.01	0.01

<sup>§</sup> Measured over 0 to 7 days.

In contrast, leach results for Synroc containing JW-K waste are comparable to those from reference Synroc.

The results of this study suggest that the use of potassium rather than sodium in reprocessing would have the potential to allow higher waste loadings in Synroc. Waste loadings might be further increased by fine-tuning the Synroc formulation so that more hollandite is formed at the expense of perovskite and zirconolite.

### 3.4 Fabrication of Cm-doped JW Synroc

For curium doping, a 1.48 g curium source (as dioxide) with a total  $\alpha$ -activity of 1.90 TBq and <sup>244</sup>Cm activity of 1.89 TBq was available. This curium source was incorporated into 91.7 g of Synroc, giving a <sup>244</sup>Cm content of 0.69 wt% in the final product. This loading was based on using 10 wt% of JW-A waste [Banba *et al.*, 1982], and the requirement to simulate a maximum disposal time of 10<sup>5</sup> years in about 2 years.

The curium source contained approximately equal quantities of <sup>240</sup>Pu (daughter of <sup>244</sup>Cm). Consequently, the curium and plutonium elements needed to be substituted for all the actinides and heavier rare earth elements in the simulated JW-A waste on a mole basis. Table 3.4.1 shows the composition of the simulated JW-A waste, including partial substitution by the curium. From this substitution, curium-doped Synroc had 10.59, 87.42 and 1.99 wt% of the simulated JW-A waste, precursor and titanium metal, respectively. (The composition of the precursor, prepared using the hydroxide route, is shown in Table 3.4.2 and full details of the preparation of the Cm-doped samples containing simulated JW-A waste are given in Mitamura *et al.* [1989] and Mitamura *et al.* [1990].)

**TABLE 3.4.1**  
**Composition of the Simulated JW-A Waste (with the substitution by Pu and Cm)**

Component	Content (wt%)	Component	Content (wt%)
<b>Fission Products</b>		<b>Fission Products</b>	
SeO <sub>2</sub>	0.10	La <sub>2</sub> O <sub>3</sub>	2.48
Rb <sub>2</sub> O	0.60	CeO <sub>2</sub>	4.95
SrO	1.66	Pr <sub>6</sub> O <sub>11</sub>	2.43
Y <sub>2</sub> O <sub>3</sub>	0.98	Nd <sub>2</sub> O <sub>3</sub>	2.24
ZrO <sub>2</sub>	8.05	Sm <sub>2</sub> O <sub>3</sub>	15.24 as (CmO <sub>2</sub> + PuO <sub>2</sub> )
MoO <sub>3</sub>	8.49	Eu <sub>2</sub> O <sub>3</sub>	
MnO <sub>2</sub>	1.26	Gd <sub>2</sub> O <sub>3</sub>	
RuO <sub>2</sub>	4.78		
Rh <sub>2</sub> O <sub>3</sub>	0.99	<b>Uranium and Actinides</b>	
PdO	2.61	CeO <sub>2</sub>	
Ag <sub>2</sub> O	0.14	<b>Process Chemicals</b>	
CdO	0.15	Na <sub>2</sub> O	15.60
SnO <sub>2</sub>	0.09	P <sub>2</sub> O <sub>5</sub>	1.58
Sb <sub>2</sub> O <sub>3</sub>	0.02	<b>Corrosion Products</b>	
TeO <sub>2</sub>	1.11	Fe <sub>2</sub> O <sub>3</sub>	13.05
Cs <sub>2</sub> O	4.79	Cr <sub>2</sub> O <sub>3</sub>	1.89
BaO	3.07	NiO	1.65
		<b>TOTAL</b>	<b>100.00</b>

**TABLE 3.4.2**  
**Composition of Curium-doped Synroc**

Component	Content (wt%)
<b>Precursor</b>	
TiO <sub>2</sub>	62.24
CaO	9.70
ZrO <sub>2</sub>	5.95
BaO	4.81
Al <sub>2</sub> O <sub>3</sub>	4.72
Subtotal	87.42
Titanium (metal)	1.99
Simulated JW-A waste (oxide)	10.59
<b>TOTAL</b>	<b>100.00</b>

### 3.5 Phase Chemistry Studies of Cm-doped JW Synroc

Solid samples of the curium-doped Synroc were examined using X-ray diffractometry. Some of the half disk specimens were annealed at 800°C for 12 hours in a closed graphite crucible (see Section 2.3) prior to the X-ray measurements. Typical results for the curium-doped samples showed the presence of freudenbergite and lovingite in addition to the hollandite, perovskite and zirconolite. When a sample that had accumulated an  $\alpha$ -decay dose corresponding to 10,000 years of storage was compared with the same material after annealing, X-ray patterns indicated that the peak intensities of the perovskite and zirconolite in the as-damaged sample are reduced far more than those of hollandite and freudenbergite. This indicates that, as expected, the short-range ( $\sim 10$  nm)  $\alpha$ -recoils cause most damage to the phases that contain the actinide elements.

### 3.6 Physical Properties of the Cm-doped JW Synroc

The densities of each of the four curium-doped Synroc samples are given in Table 3.6.1. Each value is the mean of more than six measurements made one month after hot pressing. By that time, these samples had been subjected to a cumulative dose of  $7.1 \times 10^{16}$   $\alpha$ -decays per gram, which corresponded to a Synroc age of about 20 years. The average density of the four blocks is  $4.305 \text{ g cm}^{-3}$ . The scatter in the measured values is less than 0.07% of the mean value, indicating an acceptable degree of reproducibility in hot pressing.

**TABLE 3.6.1**  
**Densities of Curium-doped Synroc**

Block Number	Density ( $\text{g cm}^{-3}$ )	Standard Deviation
1 (S87005)	4.303	0.002
2 (S87006)	4.308	0.001
3 (S87007)	4.305	0.003
4 (S87011)	4.302	0.002
Average	4.305	

Density measurements were made at intervals over a period corresponding to a Synroc age of 100,000 years. The dependence of density,  $d$ , on the cumulative  $\alpha$ -decays up to about 5,000 years is fitted by the following equation:

$$(d_0 - d) = (d_0 - d_s)(1 - e^{-kD})$$

where  $d_0$  and  $d_s$  are the initial and the saturated densities respectively,  $k$  is a constant related to damaged mass per  $\alpha$ -decay, and  $D$  is the cumulative  $\alpha$ -decays per gram.

The experimental data are shown in Figure 3.6.1 and follow the above equation with  $d_0$  and  $d_s$  equal to  $4.3069 \pm 0.0015$  and  $3.8414 \pm 1.0 \text{ g cm}^{-3}$  respectively, and  $k$  equal to  $(1.4 \pm 3.2) \times 10^{-19} \text{ g. } \alpha\text{-decay}^{-1}$  up to 5,000 years where the reduction in density is 1.0%. Beyond this point the decrease in density appears to accelerate and deviates from the above

equation to give a total reduction in density of 3.3% at the equivalent of 100,000 years. This increase in the rate of density change could be associated with the formation of cracks in the higher dose samples.

Alpha-autoradiography was carried out by exposing a 1.8-mm-thick plastic film for 10 to 15 seconds under the polished samples. A 20  $\mu\text{m}$  thick film of polyvinyl chloride was placed between the plastic film and the sample to protect the former from contamination. Photomicrographs of the  $\alpha$ -particle tracks in the plastic film were taken and analysed in an automatic image processing apparatus to determine the  $\alpha$ -track density. The results showed that, apart from some micropores and small areas containing agglomerates of reduced titanium oxides, there was a uniform distribution of  $\alpha$ -tracks on a scale of 20  $\mu\text{m}$  and above.

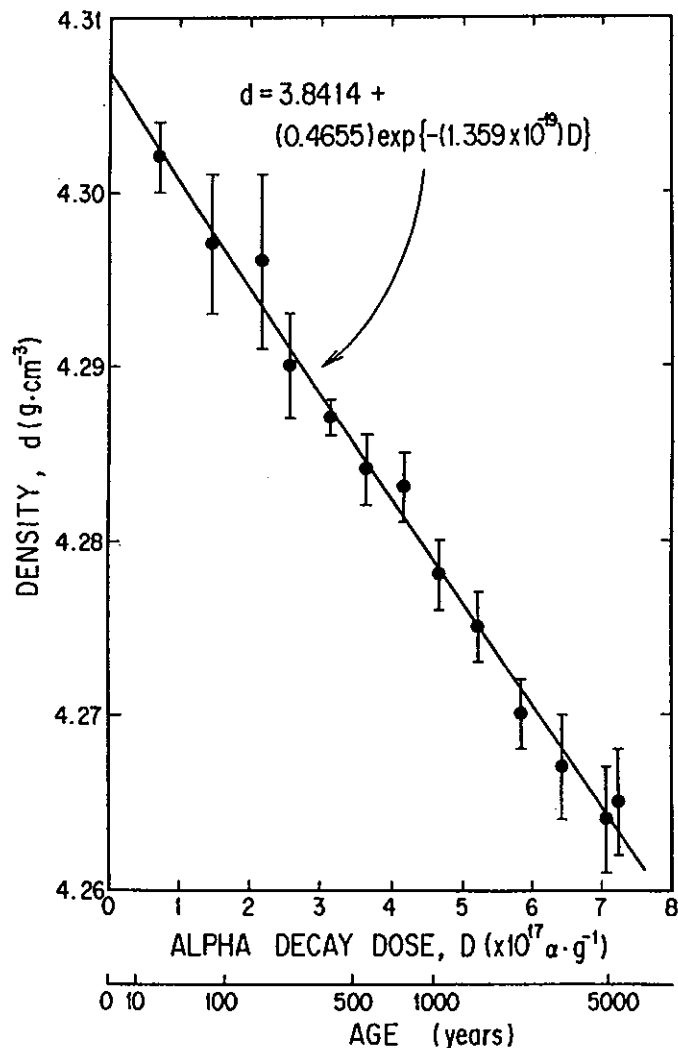


Figure 3.6.1 Density of curium-doped Synroc versus cumulative  $\alpha$ -decays. The equivalent age of Synroc containing 10 wt% of commercial waste is also shown.

### 3.7 Leaching Behaviour of the Cm-doped JW Synroc

Leaching tests on Synroc doped with  $^{244}\text{Cm}$  were carried out in WASTEF's facilities at Tokai. Analyses of inactive elements were made using ICP/AES, and curium leach rates were determined on the total sample by  $\gamma$ -spectrometry [Mitamura *et al.*, 1989]. Figure 3.7.1 shows the leach rate of the inactive elements as a function of equivalent Synroc age.

The increase in leach rate with radiation damage is apparent from the comparison of the leach rates of the indicator elements in the 140- and 33,000-year samples. The leach rates of Na and Cs increased by a factor of 10 between these samples. As these elements were contained in the actinide-free phases this increase in leach rates was probably associated with the increase in effective surface area arising from crack propagation (see Section 3.6). On the other hand, the leach rates of Sr and Ca increased by about a factor of 100 over the same equivalent storage time. This larger increase appears to be the result of the deterioration of the actinide-host phases due to  $\alpha$ -recoil damage.

Average curium leach rates from the 12,000-, 33,000-year and 109,000 samples are lower than those of the 140-year samples by between factors of 4 and 200 (see Figure 3.7.2). The reduction in leach rate was associated with the increase in pH of the leachants (see Figure 3.7.3).

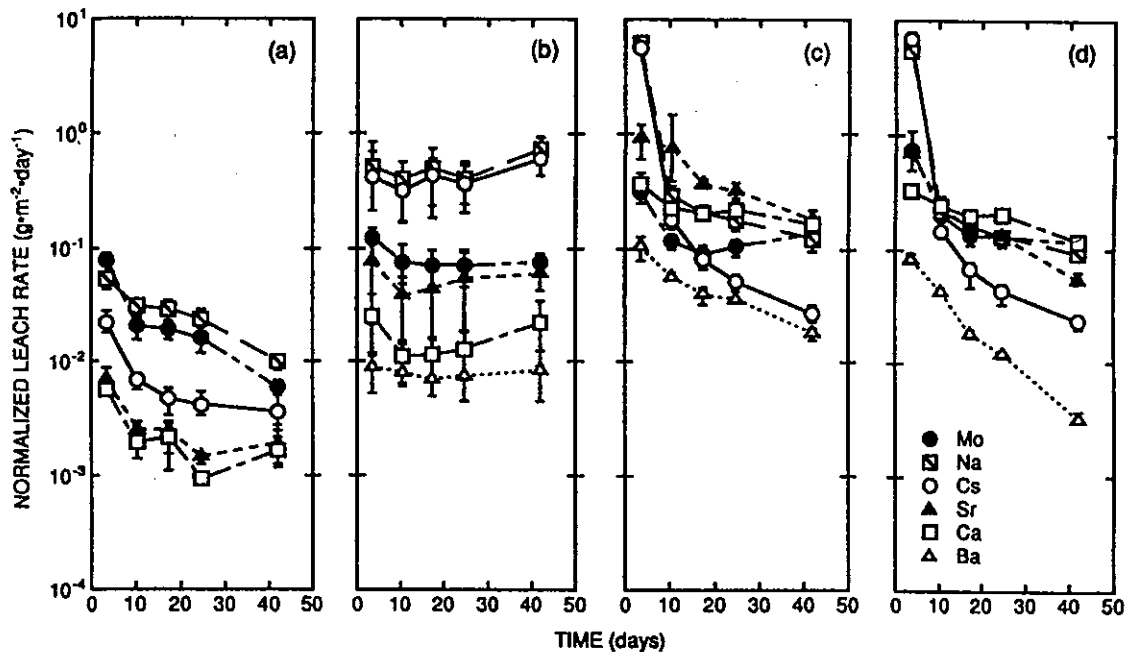


Figure 3.7.1 Normalised leach rates of inactive elements from Cm-doped Synroc with leach time. (a), (b) (c) and (d) correspond to equivalent ages of 140, 1,200, 33,000 and 109,000 years. Error bars attached to the average indicate the largest and smallest values among the three sets of specimen-charged data.

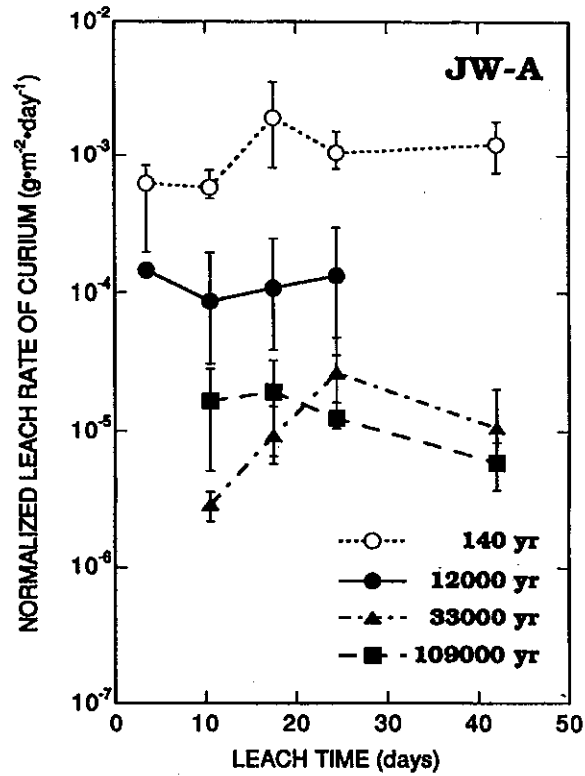


Figure 3.7.2 Normalised leach rate of <sup>244</sup>Cm with leach time. Error bars attached to the average indicate the largest and smallest values among the three sets of specimen-charged data.

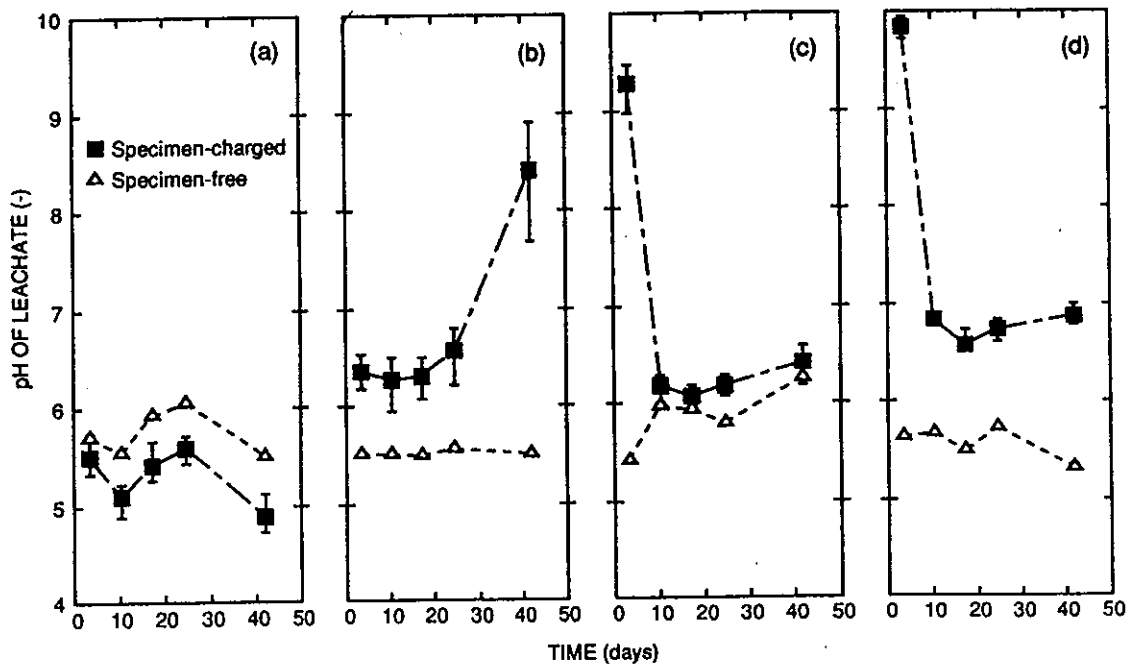


Figure 3.7.3 Change in pH of leachate from curium-doped Synroc with leach time. (a), (b) (c) and (d) correspond to equivalent ages of 140, 12,000, 33,000 and 109,000 years. Error bars are as above.

### 3.8 Effect of the Level of Cm-doping on Leach Rates from JW Synroc

For the study of radiation stability of Synroc, actinide doping method has been used to accelerate  $\alpha$ -decay damage on Synroc. However, this level is several orders of magnitude higher than actual Synroc containing high level waste. In addition, the Cm leach rate of low Cm-doping level (<0.04 wt%) at ANSTO was ~100 times lower than that of the higher Cm-doping level (~1 wt%) (see Section 2.6). Therefore, to clarify a Cm-doping effect on the Cm leach rate, six different Cm-doping levels (0.03-0.86 wt%) were selected and leach tested.

A curium source of 0.86 g was dissolved in concentrated nitric acid, together with a small amount of hydrofluoric acid. The curium solution was divided into six portions and then mixed with the same amount of the precursor (90 wt%) and JW-A simulant (10 wt%) slurry. Each mixture was calcined at 750°C for 2 hours under a stream of Ar-4%H<sub>2</sub> gas. The calcine was mixed with 2 wt% of titanium metal powder (<44  $\mu$ m) and hot-pressed at 1200°C and 29 MPa for 2 h. The overall composition of the Cm-doped samples is shown in Table 3.8.1.

The densities of polished cylindrical samples (2 cm dia. and ~1 cm thick) were measured by the water displacement method at 30°C. Polished half-disk, duplicate specimens were MCC-1 leach tested in pure water at 90°C for 2 months over four 7-day and one 28-day periods. The ratio of surface area to leachant volume was 10 m<sup>-1</sup>. After 2 cm<sup>3</sup> of leachate was collected for pH and Eh measurement, 0.1 cm<sup>3</sup> of concentrated nitric acid was added to the remainder to minimise adsorption of <sup>244</sup>Cm on the vessel wall. The total <sup>244</sup>Cm activity leached from Cm-doped specimens was measured by  $\gamma$ -ray spectrometry [Mitamura *et al.*, 1990]. When the total <sup>244</sup>Cm activity leached was below the detection limit of this method,  $\alpha$ -ray spectrometry was applied to the separated  $\alpha$  samples: particles, leachate, and acid wash solution of Teflon leach vessel.

Figure 3.8.1 shows the dependence of density on Cm source content. The density linearly increases with Cm source content increasing by 2.3 % for an increase in Cm source content of 3 wt%.

TABLE 3.8.1  
Composition of Cm-doped JW-A Synroc Samples

No.	Cm source content (wt%)	Cm content (wt%)	Waste content (wt%)
1	0.105	0.031	10.09
2	0.166	0.049	10.15
3	0.334	0.098	10.30
4	0.667	0.195	10.60
5	1.320	0.387	11.19
6	2.917	0.855	12.62

Figure 3.8.2 summarises the variation in Cm leach rate for each leach period as a function of the Cm content of Cm-doped Synroc. Roughly speaking, the average Cm leach rate gradually increases with an increase in the Cm content and reaches  $\sim 10^{-3}$  g m<sup>-2</sup> day<sup>-1</sup>. This value is similar to JAERI's results obtained from the previous  $\alpha$  acceleration tests. Although Figure 3.8.2 shows some dependence of Cm leach rate on the Cm content, the large gap in the Cm leach rate between lower and higher Cm content cannot be explained in the present study. Therefore, it is possible that other factors may contribute the increase in the Cm leach rate.

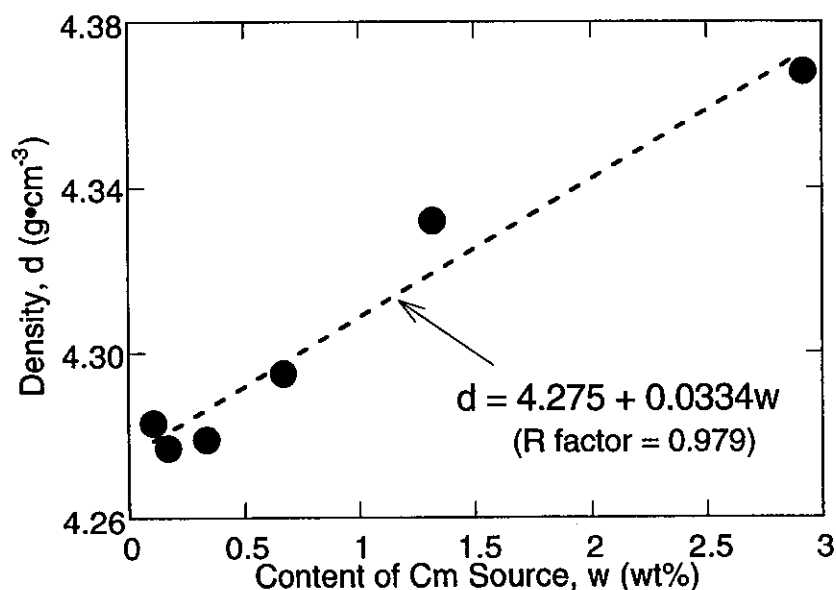


Figure 3.8.1 Change in density, d, of Cm-doped Synroc versus Cm source content, w.

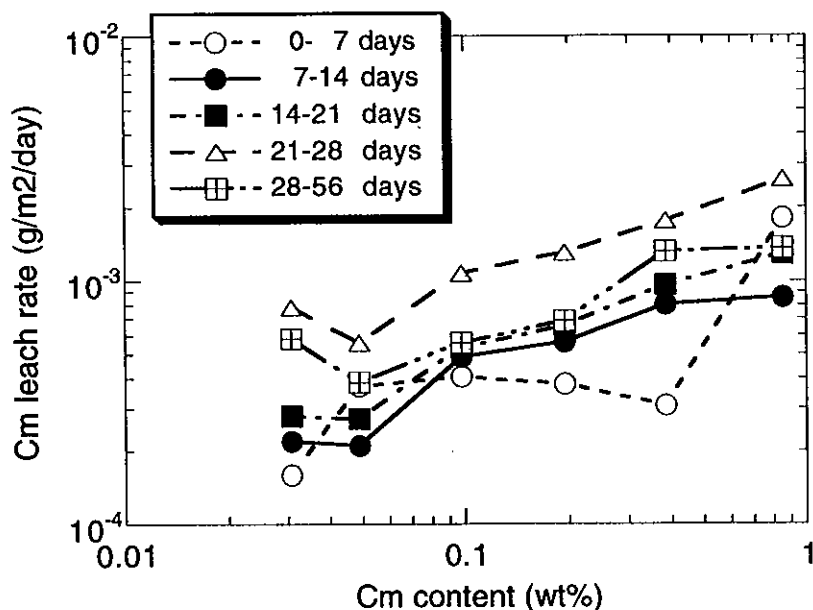


Figure 3.8.2 Effect of Cm-doping levels on Cm leach rate

## 4. MODIFICATION OF REFERENCE SYNROC TO ACCOMMODATE HIGH LOADINGS OF TRU WASTE

### 4.1 Background

In the future, actinide-rich wastes could arise from reprocessing options being considered by some countries, including Japan. As zirconolite, is the most durable phase in reference Synroc and is the primary host for actinides, a zirconolite-rich Synroc formulation was developed to incorporate high loadings of TRU.

### 4.2 Phase Chemistry Studies of Zirconolite-Rich Synroc

#### 4.2.1 Non-radioactive specimens

Earlier studies on the incorporation of Nd, U, Np, into synthetic zirconolites were not always specific about valence states or substitution mechanisms [Fielding and White, 1987; Smith and Lumpkin, 1993; Kesson *et al.*, 1983; Vance and Agrawal, 1982; Clinard *et al.*, 1982; Clinard *et al.*, 1984; Matzke *et al.*, 1988; Matzke *et al.*, 1990; Smith *et al.*, 1993]. In this part of the collaborative program carried out at ANSTO, the valence state of selected substitutions of multivalent ions in zirconolite was investigated by a well-known strategy of synthesis. The basic concept is to model a particular substitution mechanism by synthesising a zirconolite that exhibits that particular substitution. If the experimental products are essentially single-phase zirconolites, then the nature and existence of that substitution mechanism are thereby confirmed.

Initially, aqueous nitrate solutions of Ca, rare earths or actinides and any charge compensating ions such as Al, that were deemed necessary were mixed together. After stir-drying, the mixtures were calcined in air (for rare earths) or 3.5% $H_2/N_2$  (for actinides) at  $\sim 700^\circ C$  to remove water,  $NO_x$  and organics. Final consolidation and equilibration of the rare-earth-containing samples was achieved by pelletising and sintering for 1-3 days at  $1350-1400^\circ C$ , with some intermediate grinding and re-sintering steps. While these temperatures are higher than those envisaged in Synroc production, the objective was to achieve equilibration by prolonged heating within  $\sim 100^\circ C$  of the melting point ( $1525^\circ C$  for pure  $CaZrTi_2O_7$  [Vance *et al.*, 1992]). Consolidation of the actinide-bearing samples was achieved by hot-pressing in graphite dies of 1 cm bore at  $1250^\circ C/18$  MPa for 2h to yield two 2 mm thick samples per pressing. (A disadvantage of hot-pressing in graphite is that the reducing conditions stabilise some titanium in the trivalent state and thereby result in the formation of a minor fraction of perovskite.) The hot-pressed samples were reheated in air or neutral conditions to enhance equilibration.

XRD was carried out with conventional diffractometers on powdered rare-earth-containing samples, U-bearing samples were in the form of 1 cm diameter hot-pressed or sintered pellets, and the Np- and Pu-bearing samples consisted of hot-pressed pellets cut in half along their diameters, set in a resin, and finally polished to a finish of  $1 \mu m$ . SEM and TEM were used to characterise polished pellets and ion-thinned materials as appropriate.

**Neodymium.** To investigate the solubility of  $\text{Nd}^{3+}$  in the Ca site of zirconolite, samples of  $\text{Ca}_{(1-x)}\text{Nd}_x\text{ZrAl}_{(x)}\text{Ti}_{(2-x)}\text{O}_7$  were fabricated. Samples with  $x \leq 0.65$  were essentially single-phase but additional phases such as alumina and zirconia were observed for  $x > 0.7$ . AEM analysis of the  $x = 0.5$  specimen showed that the material was of the 2M polytype.

Samples were also prepared with  $(\text{Ca}_{(1-x)}\text{Nd}_x)(\text{Nd}_x\text{Zr}_{(1-x)})\text{Ti}_2\text{O}_7$  stoichiometry and it was concluded that the solid solubility of  $\text{Nd}^{3+}$  in the Zr site was at most 0.2 formula units.

Finally, samples were prepared with  $\text{Ca}(\text{Nd}_x\text{Zr}_{(1-x)})\text{Ti}_2\text{O}_7$  stoichiometry to see if Nd could be incorporated as  $\text{Nd}^{4+}$ . No such solubility was deduced and XANES studies showed no evidence for Nd in valence states other than  $\text{Nd}^{3+}$ .

**Cerium.** The valence state and crystal chemistry of cerium in zirconolite was characterised as follows: if Ce-1 of nominal composition  $\text{Ca}_{0.8}\text{Ce}_{0.2}\text{ZrTi}_{1.8}\text{Al}_{0.2}\text{O}_7$ , yielded a single-phase zirconolite, then it would imply that Ce was trivalent and substituted on the Ca site, with  $\text{Al}^{3+}$  as a charge compensator on a Ti site. XRD and SEM confirmed this to be the case, albeit only under reducing conditions. When synthesis was conducted in air, the Ce was approximately equally stabilised in the +3 and +4 states. TEM and positron annihilation lifetime studies have indicated that charge balance is satisfied by Ce or Ti vacancies [Begg *et al.*, 1998, Hadley *et al.*, 1998].

By analogy if samples Ce-2 and Ce-3 of nominal compositions  $\text{Ca}_{0.8}\text{Ce}_{0.2}\text{ZrTi}_{1.6}\text{Al}_{0.4}\text{O}_7$  and  $\text{CaZr}_{0.8}\text{Ce}_{0.2}\text{Ti}_2\text{O}_7$  yielded single-phase products then those zirconolites would therefore contain tetravalent Ce, substituting in the Ca or Zr sites respectively.

Ce-1 was found to be essentially single-phase zirconolite from XRD and SEM studies. Thus it was concluded that coupled substitution of  $\text{Ce}^{+3} + \text{Al}^{3+}$  for  $\text{Ca}^{2+} + \text{Zr}^{4+}$  allows  $\text{Ce}^{3+}$  to enter into Ca site. Further X-ray absorption spectroscopy however showed that this was so, only under reducing conditions. Ce-2 contained alumina in addition to zirconolite, whilst Ce-3 contained two zirconolites, one of which was relatively low in Ce and the other (possibly a pyrochlore) was relatively enriched. It is concluded that perhaps some, but certainly not all, of the Ce was tetravalent. Indeed our results for Ce-3 were similar to earlier results by Clinard [1984] for an analogous Pu-doped composition [Matzke *et al.*, 1990]. A set of samples of composition  $\text{Ca}_{(1-x)}\text{Ce}_x\text{ZrTi}_{(2-x)}\text{Al}_{(x)}\text{O}_7$  gave XRD results which were broadly similar to the analogous Nd-doped series described above and implied extensive solid solubility of  $\text{Ce}^{3+}$  (and  $\text{Ce}^{4+}$ ) in the Ca site of zirconolite.

#### 4.2.2 Radioactive specimens

**Uranium.** Our syntheses were designed to demonstrate either (a)  $\text{U}^{4+}$  substituting on the Zr site using a composition equivalent to  $\text{CaU}_x\text{Zr}_{1-x}\text{Ti}_2\text{O}_7$  and (b)  $\text{U}^{4+}$  substituting in the Ca site, along with two  $\text{Al}^{3+}$  ions replacing  $\text{Ti}^{4+}$  for charge compensation. Here a composition equivalent to  $\text{Ca}_{(1-x)}\text{U}_x\text{ZrAl}_{(2x)}\text{Ti}_{(2-2x)}\text{O}_7$  was used.

The samples of nominal composition  $\text{CaZr}_{(1-x)}\text{U}_x\text{Ti}_2\text{O}_7$  showed that the transformation from the zirconolite structure to pyrochlore occurred at an  $x \sim 0.5$  with equilibration being assisted by short ( $\approx 2$  hours) heat-treatments at  $1300^\circ\text{C}$  after hot-pressing, to remove metastable perovskite etc. However it was found that prolonged heating (for about 20 h) caused severe disproportionation. This anomaly was not pursued, as it seemed to require temperatures/times well outside reasonable limits for Synroc hot-consolidation. More recent syntheses using

sintering in an argon atmosphere has shown that for compositions of  $\text{CaU}_x\text{Zr}_{1-x}\text{Ti}_2\text{O}_7$  the zirconolite 2M phase exists for  $x$  values up to 0.15, while the 4M variety is present from  $0.2 < x < 0.5$ , and that the zirconolite - pyrochlore boundary lies at  $x \sim 0.6$ .

The other composition ( $\text{Ca}_{(1-x)}\text{U}_{(x)}\text{ZrAl}_{(2x)}\text{Ti}_{(2-2x)}\text{O}_7$ ) did not display disproportionate effects on heating in the 1300-1400°C range, and it was concluded that the  $\text{U}^{4+}$  solubility in the Ca site of zirconolite corresponded to  $x = 0.2-0.3$ . Additional phases stabilised at  $x > 0.4$  were mainly  $\text{UO}_2\text{-ZrO}_2$  solid solutions and alumina. However, no evidence was found by XANES or diffuse reflectance spectroscopy on powder samples for  $\text{U}^{5+}$  or  $\text{U}^{6+}$  even when suitable charge compensators were present.

**Neptunium and Plutonium.** The specimen compositions and targeted actinide valencies are summarised in Table 4.2.1. XRD and SEM results are summarised in Table 4.2.2. Nearly single-phase zirconolites with the nominal formula given below were successfully synthesised at 1300°C, demonstrating the flexibility of the zirconolite structure to accommodate these nuclides in different sites by a variety of single and coupled solid solution mechanisms.

**TABLE 4.2.1**  
**Model Valencies/site Locations for Np and Pu in Zirconolites**

Sample	Bulk Composition	Valence	Site
Np-1	$\text{Ca}_{0.8}\text{Np}_{0.2}\text{ZrTi}_{1.8}\text{Al}_{0.2}\text{O}_7$	+3	Ca
Np-2	$\text{CaZr}_{0.8}\text{Np}_{0.2}\text{Ti}_2\text{O}_7$	+4	Zr
Pu-1	$\text{Ca}_{0.8}\text{Pu}_{0.2}\text{ZrTi}_{1.8}\text{Al}_{0.2}\text{O}_7$	+3	Ca
Pu-2	$\text{CaZr}_{0.8}\text{Pu}_{0.2}\text{Ti}_2\text{O}_7$	+4	Zr

**TABLE 4.2.2**  
**Phase Assemblages from XRD and SEM for Hot-pressed Np- and Pu-doped Zirconolites, Before and After Heat-treatment**

Sample	Heat-treatment	(wt%)				
		Zirconolite	"Pyrochlore"	Perovskite	Rutile	Zirconium
Np-1	-	100				
	H1	89			8	3
	H2	89			8	3
Np-2	-	80		20		
	H1	93*	7	<1	<1	
	H2	93	7	<1	<1	
Pu-1	-	85		15		
	H1	100				
	H2	95		5		
Pu-2	-	70		30		
	H1	90	10		<1	
	H2	88	7		5	

H1 and H2 2 h at 1300°C in air or nitrogen respectively.

\* Small peak observed at d spacing of  $2.84 \pm 0.01$  Å due to the 4M zirconolite polytype, very similar to the result obtained for Ce-3 above

The key conclusion [Vance *et al.*, 1994 Actinides 93] from the XRD results was that, given the >90% abundance of zirconolite in all the heated samples, that for both Np and Pu, both trivalent and tetravalent cations are readily stabilised and accommodated under standard fabrication conditions.

In the Np-2 and Pu-2, Al-free formulations SEM analyses of the zirconolites show that Np and Pu contents are less than those of the model compositions. These zirconolites coexist with a significant fraction of a more actinide-rich, pyrochlore-like phase. These results indicate that the solubility limits for Np and Pu in zirconolite have been exceeded, just as for Ce-3. Thus only about 0.15 to 0.17 cations per formula unit of Np or Pu are accommodated if there is no compensatory cation (e.g. Al<sup>3+</sup>) present. In contrast, zirconolites in the Al-bearing Np-1 and Pu-1 formulations, phase assemblages and compositions are the same whether they were heated in air or nitrogen, while nitrogen favours the entry of Pu into the Ca site in the presence of charge-balancing aluminium.

TEM studies of Np-2 confirmed the corresponding SEM studies, and the high-resolution lattice images showed the zirconolite crystallites (2M polytype) to be almost free of defects. Key results are shown in Table 4.2.3.

The crystal chemistry of Np, however, is subtly different from that of Pu and Ce. Experiments at the Stanford synchrotron facility in December, 1995 showed that Np<sup>3+</sup> is stabilised only under extremely reducing conditions (graphite dies, at high temperatures) and that the most commonly-adopted Np valence was Np<sup>4+</sup> [Begg *et al.*, 1998 MRS 1997].

**TABLE 4.2.3**  
**Solid Solubility (formula units) Limits of REE + actinides in Zirconolite,**  
**Deduced from XRD and SEM studies.**

RE/Ac	Atom fraction	
	Ca site	Zr site
Nd <sup>3+</sup>	0.65	<0.2
Ce <sup>3+</sup>	0.65	?
Ce <sup>4+</sup>	~ 0.3 (?)	0.15
U <sup>4+</sup>	~ 0.2	0.6
Pu <sup>3+</sup>	0.4	trace
Pu <sup>4+</sup>	~ 0.3 (?)	0.15
Np <sup>3+</sup>	0.1 (?)	
Np <sup>4+</sup>	0.3 (?)	0.15

? refers to values which have high uncertainty in the quoted value or those which have not been fully ascertained.

### 4.3 Fabrication of Cm-Doped Zirconolite

For partitioned actinide-rich reprocessing wastes, a ceramic nominally composed of ≈ 80 wt% zirconolite, plus ≈ 5 wt% each of hollandite, perovskite and rutile has been studied. In this study, it was assumed that U is tetravalent, and that other actinides exist as trivalent species

on the Ca site of zirconolite.  $\text{Nd}^{3+}$  was used as a simulant for the trivalent actinides and U was added as necessary. In early work, a target waste loading of 30 wt% of an equimolar mixture of Nd and U was used, but pyrochlore formed instead of zirconolite along with considerable amounts of brannerite ( $\text{UTi}_2\text{O}_6$ ). Consequently, the waste loading was decreased to 20 wt%. (In this phase design, we have assumed an equimolar mixture of tetra and trivalent waste actinides, corresponding to a reprocessing efficiency of > 99%.)

The composition of the new zirconolite-rich ceramic is (wt%):  $\text{Al}_2\text{O}_3$  (2.6); BaO (2.4); CaO (10.0);  $\text{Nd}_2\text{O}_3$  (6.6);  $\text{TiO}_2$  (48.4);  $\text{UO}_2$  (10.4); and  $\text{ZrO}_2$  (19.6). It was hot-pressed at 1170°C and 20 MPa. The above phase assemblage was confirmed by XRD studies, although traces of brannerite were still observed. The compositional flexibility of this ceramic was such that minimal mineralogical change occurred if the waste loading was varied between 16 and 24 wt%.

Leaching experiments were carried out on these samples, plus the afore mentioned samples with 30 wt% loading. After periods of 7 and 28 days, the total (vessel wall + solution) elemental extractions agreed within an order of magnitude and lay in the ranges of ( $\text{g m}^{-2} \text{d}^{-1}$  at 90°C):  $10^{-1}$  to  $10^{-2}$  (Ca);  $10^{-2}$  to  $10^{-3}$  (Ba);  $10^{-3}$  to  $10^{-4}$  (Nd);  $10^{-2}$  (Al);  $10^{-4}$  to  $10^{-5}$  (U);  $10^{-6}$  (Ti); and  $10^{-7}$  (Zr). The leach rates decreased with time, and were comparable with equivalent values for reference-grade Synroc-C.

From the work carried out at ANSTO in developing a precursor for actinide-doped zirconolite (as detailed in Section 4.2 and above) a set of samples was prepared assuming the actinides in the Cm-source to be trivalent and to be incorporated in the calcium site via coupled substitution of  $\text{Al}^{3+}$  for  $\text{Ti}^{4+}$ , i.e.;



(However, this is an approximation to the true state of affairs because some  $\text{Ti}^{3+}$  could be stabilised, as a result of the reducing conditions imposed by the use of graphite dies. A small amount of  $\text{Al}^{3+}$  thereby being displaced.)

The Cm used in this study contained 37 mole% of  $^{244}\text{Cm}$ , and 58 mole% of its daughter  $^{240}\text{Pu}$  on May 24, 1994. A 0.8403 g sample of the Cm was dissolved in 45 g of concentrated nitric acid with 0.1  $\text{cm}^3$  of hydrofluoric acid (47%), and then 10  $\text{cm}^3$  of 0.1N nitric acid was added to decrease the loss of the Cm source during subsequent processing. The Cm source was mixed with 41.6 g (oxide equivalent) of slurry precursor that consisted of 0.12027, 0.12341, 0.00314 and 0.24368 moles of calcium, zirconium, aluminium, and titanium, respectively.

The pH of the slurry mixture was adjusted to 9 with ammonium hydroxide. The slurry mixture was then poured into an in-cell calciner pot, dried at 80°C, and then calcined at 750°C for 2 hours in a stream of air. The powder (41.0794 g) was collected from the calciner pot (recovery was 96.9%). The pour and tap densities of the calcined powder were measured before dividing it into three; i.e. 13.6998, 13.5457, and 13.8666 g, then each was hot-pressed using a graphite die at 1200°C and 29 MPa for 2 hours in a stream of  $\text{N}_2$  gas.

#### 4.4 Physical Properties of Cm-Doped Zirconolite-Rich Synroc

Pour and tap densities of the calcined powder were  $0.62 (\pm 0.01)$  and  $1.19 (\pm 0.01 \text{ g.cm}^{-3})$ . The values in parentheses represent the standard deviation from seven measurements. The change in density of the cylindrical monoliths of the Cm-doped zirconolite-rich monoliths is shown in Figure 4.4.1 together with data for Cm-doped, reference Synroc containing Na-free (PW-4b) and Na-bearing simulated high-level waste, and Cm-doped perovskite. The density changes are well fitted by linear extrapolation. At a dose of  $3 \times 10^{17} \alpha\text{-decays.g}^{-1}$ , the fractional density decrease of the Cm-doped zirconolite-rich formulation was 0.4%. In Figure 4.4.1 the slope of the fitted line for the Cm-doped zirconolite is perhaps slightly smaller than that for Cm-doped perovskite. The data themselves agree reasonably well with those of Vernaz *et al.* [1990] for  $^{238}\text{Pu}$  and  $^{244}\text{Cm}$ -doped zirconolite.

Figure 4.4.2 shows an X-ray diffraction pattern from the Cm-doped zirconolite-rich Synroc one day after hot-pressing (dose =  $1.7 \times 10^{15} \alpha\text{-decays.g}^{-1}$ ). These data indicate that, here, the sample consisted mainly of zirconolite; it did not contain the less durable perovskite phase. However X-ray patterns from some other areas of the sample revealed that a considerable amount of additional phases, mainly rutile and zirconia, are present.

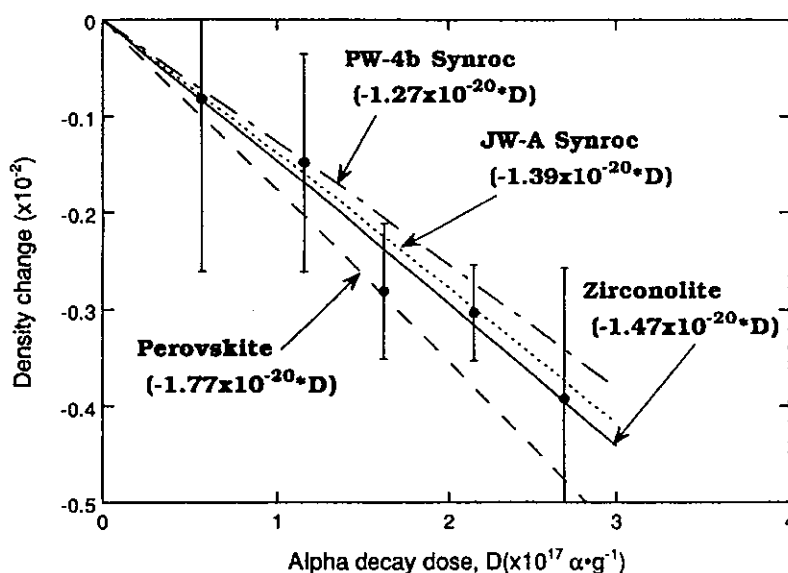


Figure 4.4.1 Change in density as a function of  $\alpha$ -decay dose for Cm-doped Synroc containing JW-A and PW-4b waste, Cm-doped zirconolite and Cm-doped perovskite.

#### 4.5 Leaching Behaviour of Cm-Doped Zirconolite-Rich Synroc

The three hot-pressed cylinders prepared as above were polished using 6- $\mu\text{m}$  diamond paste on flat faces and #600 grit abrasive paper on the peripheries. Two of the cylinders, Z94002 and Z94003 were sliced and then cut across their diameters to make half-disk specimens for leach testing. Two half-disk specimens that had accumulated a dose of  $1.5 \times 10^{17} \alpha \text{ decays.g}^{-1}$  were MCC-1 leach tested in pH  $\sim 2$  solution (0.05M KCl + 0.013M HCl) at  $90^\circ\text{C}$  for two months over four 7-day plus one 28-day leach periods. The leachate samples were analysed by  $\gamma$ -ray spectrometry for  $^{244}\text{Cm}$  and ICP-AES for Ca.

The normalised leach rate results of  $^{244}\text{Cm}$ , and changes in pH with time, are shown in Figure 4.5.1. This Figure also shows a comparison between data collected for zirconolite and perovskite collected under similar leaching conditions. The leach rates of the two materials are different at late stages of the first month, but similar in the final leaching run due to lower Cm solubility in the higher-pH, perovskite leachate.

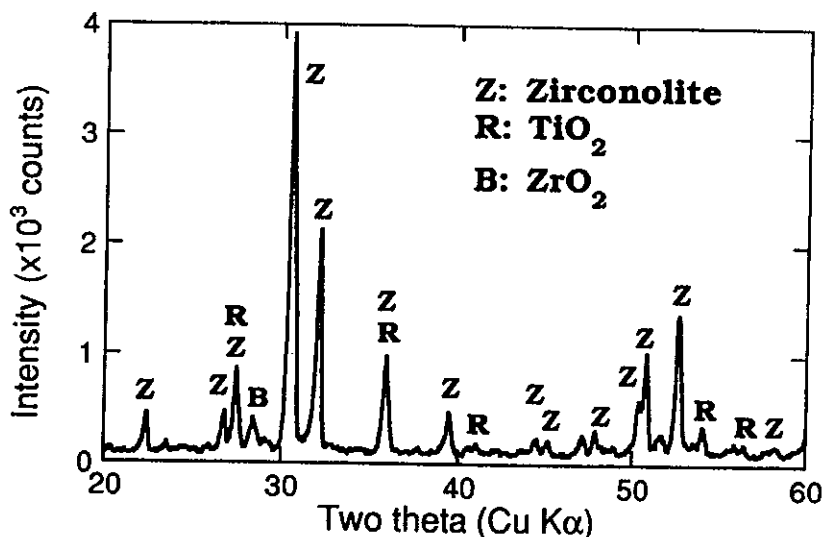


Figure 4.4.2 XRD pattern for Cm-doped zirconolite (dose =  $1.7 \times 10^{15}$   $\alpha$ -decays.g $^{-1}$ ).

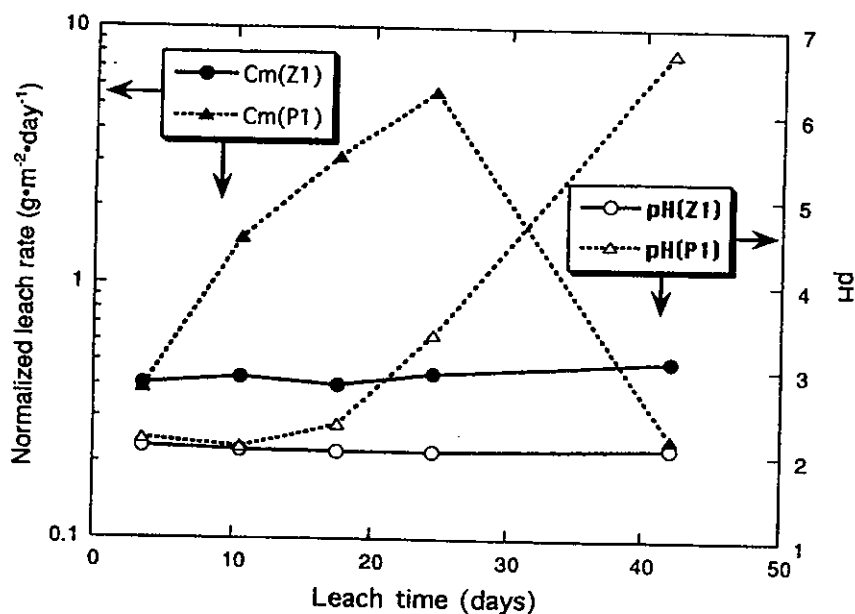


Figure 4.5.1 Normalised leach rate of  $^{244}\text{Cm}$  and pH versus leach time. (Z1 & P1 stand for Cm-doped zirconolite and perovskite, respectively.)

## 5. FUNDAMENTAL STUDIES OF TRU IMMOBILISATION MECHANISMS

### 5.1 Background

The ability of the Synroc matrix to contain TRU elements has been demonstrated mostly in relatively short-term (1 to ~ 2500 days) leaching studies. Consequently, in order to extrapolate these results to the performance of the waste form under repository conditions over geological time, it is necessary to understand and model the leaching behaviour of Synroc. To further this objective, leaching studies of nominally single-phase powders, natural analogues of Synroc phases and extended duration leaching tests (>200 days) have been utilised.

### 5.2 Leaching Studies

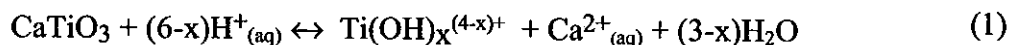
Studies of Synroc dissolution under repository conditions are being conducted for times which are as long as practicable, so that real-time data can then be extrapolated on chemically-defensible grounds to time-scales of at least  $10^4$  years. Recent results from the leaching of individual, Synroc phases, and the long-term data for  $^{134}\text{Cs}$  are reported below.

#### 5.2.1 Long-term leaching studies

The slow reaction rate of monolithic Synroc with solutions can be dealt with in laboratory experiments to a certain extent by utilising powdered samples. Work reported previously [Ringwood *et al.*, 1988] and results obtained by Van Iseghem *et al.* [1995] have shown at high surface area to volume (SA/V) ratios (i.e. using powders) that the overall releases from Synroc are dominated by initial releases, i.e. those occurring over the first day, with relatively little further dissolution occurring thereafter. At SA/V ratios greater than 1,000 there is a decrease in the solution release rates of Mo, Ba and Ca, consistent with precipitation of these elements.

Complementary studies on the individual Synroc phases to provide insight into the dissolution kinetics have been carried out. Perovskite ( $\text{CaTiO}_3$ ), doped perovskite ( $(\text{Ca}_{0.78}\text{Sr}_{0.04}\text{Nd}_{0.18})\text{Ti}_{0.82}\text{Al}_{0.18}\text{O}_3$ ) and zirconolite ( $\text{CaZrTi}_2\text{O}_7$ ) samples have been studied under flow-through conditions in pH-buffered leachants at  $90^\circ\text{C}$ . Detailed results of this study have been reported by McGlenn *et al.* [1994].

At all pHs the release of Ca was found to greatly exceed that of Ti. This result is consistent with the work of Pham *et al.* [1989]. These authors suggested that the dissolution of perovskite, at temperatures  $\leq 90^\circ\text{C}$ , in deionised water could be described by the following equation;



The presence of anatase and rutile on some of the leached perovskite and doped perovskite specimens in this study suggests that some releases might occur according to the above mechanism. However, Equation (1) describes a leaching mechanism which should be strongly dependent on pH; however our studies do not substantiate this effect. Moreover, the kinetics of leaching change with time. So although reaction (1) might correctly describe the

very short term, i.e. < 1 day performance, the longer-term release of Ca is evidently controlled by other processes.

Leaching studies of zirconolite have shown that releases of Ca are only weakly dependent on pH. The slow reaction rate of the zirconolite makes it difficult to quantify the leaching mechanisms but as Ca is released into solution in much larger quantities than Ti and Zr, it appears that mechanisms analogous to those for perovskite also control releases from zirconolite. Unfortunately SEM examination revealed no secondary phases on the zirconolite powders, and so the specific leaching mechanism remains unresolved.

The results obtained for the perovskite powders are very similar to results obtained for pH controlled experiments carried out with Np-doped Synroc [Blackford *et al.*, 1992]. With the exception of the datum measured at pH 2, the leach rate of Np is insensitive to pH with leach rates varying by less than a factor of 10 over the pH range 5.4 to 10. However when the same studies were carried out with Synroc doped individually with Am, Pu, and Cm, the effect of pH on the radionuclide leaching was much greater. The leach rates of Pu, Am and Cm were reduced by between 3 and 4 orders of magnitude between pHs of 7 and 10, reflecting the reduced solubility of these elements under alkaline conditions.

These results emphasise that not only is the matrix important for controlling the release of elements but the chemistry of the element under the repository conditions must be well known to enable leaching processes to be coupled with reliable chemistry and transport codes. Currently, our ability to describe the behaviour of radionuclides like Pu, Am and especially Cm are limited by knowledge of their solution chemistry and the limitations of thermodynamic databases.

### **5.3 Fundamental Studies on Single Phase Perovskite Samples**

#### **5.3.1 Fabrication of Cm-Doped Perovskite**

To augment the single-phase studies carried out with inactive samples at ANSTO, data were obtained for Cm-doped perovskite synthesised by JAERI using formulations supplied by ANSTO. Detailed information about the preparation of these samples is given in Mitamura *et al.* [1994].

The perovskite prepared by JAERI had a specific  $^{244}\text{Cm}$  and  $\alpha$ -activity of were 22.40 GBq.g<sup>-1</sup> (0.6053 Ci.g<sup>-1</sup>) and 22.29 GBq.g<sup>-1</sup> on 31 March, 1993.

#### **5.3.2 Physical Properties of Cm-Doped Perovskite**

**Density.** Pour and tap densities of the calcined products were 0.53 and 1.09 g cm<sup>-3</sup>. The average density of the three hot-pressed samples was 4.083 g.cm<sup>-3</sup>, one month after hot pressing when the samples had accumulated a dose of  $7 \times 10^{16}$   $\alpha$ -decays.g<sup>-1</sup>. The reduction in density of the Cm-doped perovskite cylinder, shown in Figure 5.3.1, is linear. At a dose of  $9 \times 10^{17}$   $\alpha$ -decays.g<sup>-1</sup>, the density deficit of the Cm-doped perovskite was 1.3%. This value is in fair agreement with those of Vernaz *et al.* [1990] for  $^{238}\text{Pu}$ -doped perovskite.

**XRD.** As-leached and annealed half-disk specimens were studied using XRD. Surfaces of annealed specimens were finished with 6  $\mu\text{m}$  diamond paste after 800°C annealing in graphite. XRD data were collected at intervals of 0.05° over the  $2\theta$  range of 10-120°, using Cu  $K_{\alpha}$  radiation.

Figure 5.3.2 shows X-ray diffraction patterns from annealed and as-leached specimens which had accumulated a dose of  $5.6 \times 10^{17} \alpha\text{-decays.g}^{-1}$ . The annealed specimen contained predominantly the perovskite phase although it also contained minor amounts of a phase (indicated by “\*” on the pattern), probably  $(\text{Cm,Pu})\text{O}_2$ . After leaching anatase ( $\text{TiO}_2$ ) lines are present along with those of the above phases. The precipitation of anatase is consistent with leach data, which showed low solution concentrations of Ti (see Section 5.3.3), compared to that of Ca and Cm.

### 5.3.3 Leaching Behaviour of Cm-Doped Perovskite

Leach testing of half-disk specimens was carried out in pH ~2 solution (0.05M KCl + 0.013M HCl) at 90°C [Mitamura *et al.*, 1994]. (This leachate was used for testing as it was postulated that the Cm leached from the Synroc would be soluble at this pH, but not under neutral conditions, and gross counting techniques could be used to assess the total leach rate without having to separately measure solution and vessel wall contributions to activity.) The leachate samples were analysed by  $\gamma$ -ray spectrometry for  $^{244}\text{Cm}$  and ICP/AES for non-radioactive elements.

The weight losses of half-disk specimens after two-months correspond to average leach rates of 1.7, 2.3, and 3.0  $\text{g.m}^{-2}.\text{d}^{-1}$  from the Cm-doped perovskite material that accumulated doses of  $1.6 \times 10^{17}$ ,  $4.0 \times 10^{17}$ , and  $8.3 \times 10^{17} \alpha\text{-decays.g}^{-1}$ , respectively (Table 5.3.1).

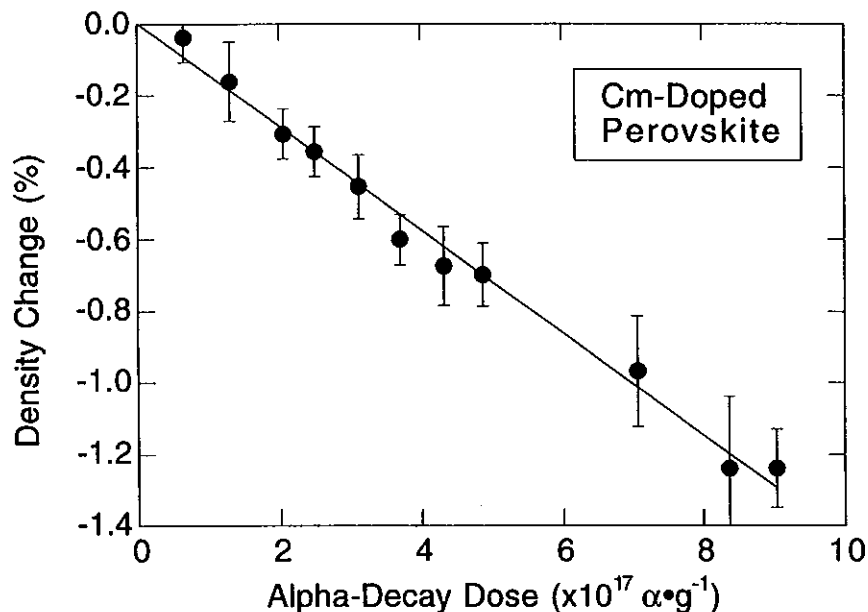


Figure 5.3.1 Change in density with increasing  $\alpha$ -decay damage for Cm-doped perovskite.

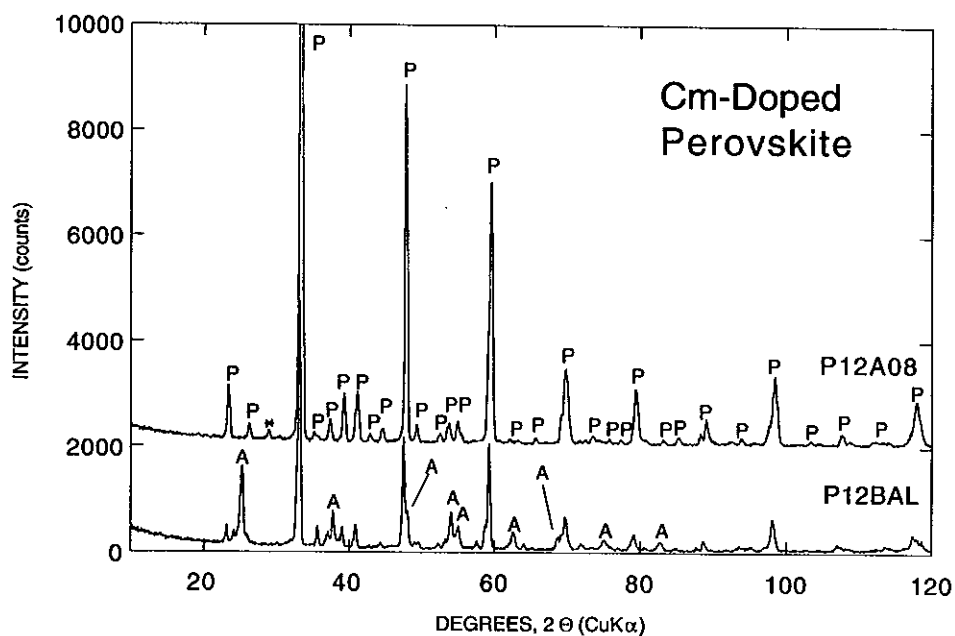


Figure 5.3.2 XRD Patterns from annealed (P12A08) and as-leached (P12BAL) Cm-doped perovskite specimens. (Cu K $\alpha$  radiation.)

**TABLE 5.3.1**  
**Leach Rates of Cm-doped Perovskite (based on CaO loss)**

Specimen Name	Leach Rate* A (g m <sup>-2</sup> d <sup>-1</sup> )	Leach Rate# B (g m <sup>-2</sup> d <sup>-1</sup> )	(A/B)x100 (%)	Dose ( $\alpha$ -decays g <sup>-1</sup> )
P1-3B	0.93	1.28	73	1.6 x 10 <sup>17</sup>
P2-2B	1.47	1.77	83	1.6 x 10 <sup>17</sup>
P2-5B	1.97	2.08	95	1.6 x 10 <sup>17</sup>
Average	1.46	1.71		
P1-2B	1.88	2.07	91	4.0 x 10 <sup>17</sup>
P1-4B	2.22	2.43	91	4.0 x 10 <sup>17</sup>
P2-3B	2.43	2.46	99	4.0 x 10 <sup>17</sup>
Average	2.18	2.32		
P1-3A	2.98	3.04	98	8.3 x 10 <sup>17</sup>
P2-2A	2.94	3.02	97	8.3 x 10 <sup>17</sup>
P2-4A	2.85	2.78	103	8.3 x 10 <sup>17</sup>
Average	2.92	2.95		

\*A Derived from CaO weight loss

#B Derived from total weight loss

**Figure 5.3.3** compares changes in the normalised Ca leach rate and pH with leaching time. In this Figure, (1), (2), and (3) indicate leaching runs after doses of  $1.6 \times 10^{17}$ ,  $4.0 \times 10^{17}$ , and  $8.3 \times 10^{17} \alpha\text{-decays.g}^{-1}$ , respectively. Unlike the normal leaching behaviour of Synroc, in which all leach rates decrease with increasing leaching time, the Ca leach rate from the Cm-doped perovskite initially increases with leach time. However it begins to fall again after  $\sim 25$  days. The more damaged specimens tend to give a higher Ca leach rate. In the 28-56 day leaching period, the acidic leachant solution was partly neutralised by  $\text{Ca}^{2+}$ -proton exchange and the Ca leach rate for the samples which had accumulated three different doses converged to a similar value. Titanium concentrations in the leachates were near the limit of detection.

The  $\gamma$ -ray spectrometry also showed high leach rates of  $^{244}\text{Cm}$  initially (**Figure 5.3.4**) and Ca and Cm leach rates were similar. However, in the final leaching period, the Cm leach rate was lower than the Ca leach rate by a factor of  $>20$ , no doubt due to the lower Cm solubility at the higher pH.

The leach rates given above for Cm-doped perovskite are higher than those measured for inactive samples at ANSTO. Work at ANSTO has shown that under the pH = 2 conditions, the enhanced leaching of the JAERI material is probably due to traces of fluoride being released from the Teflon arising either from partial disintegration caused by the acid washing procedure used for cleaning the Teflon and/or the interaction of  $\alpha$ -activity with the Teflon.

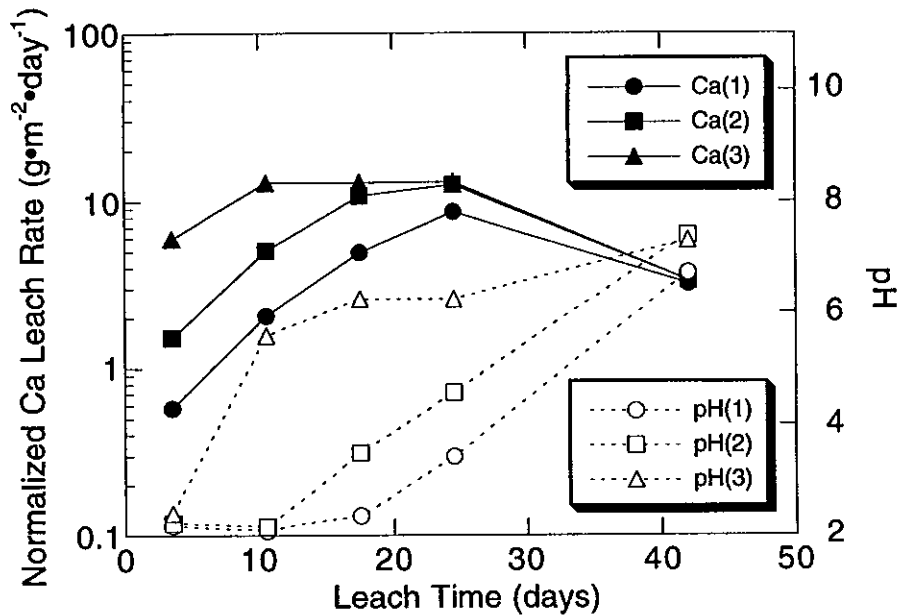


Figure 5.3.3 Comparison of the normalised Ca leach rate and pH with time.

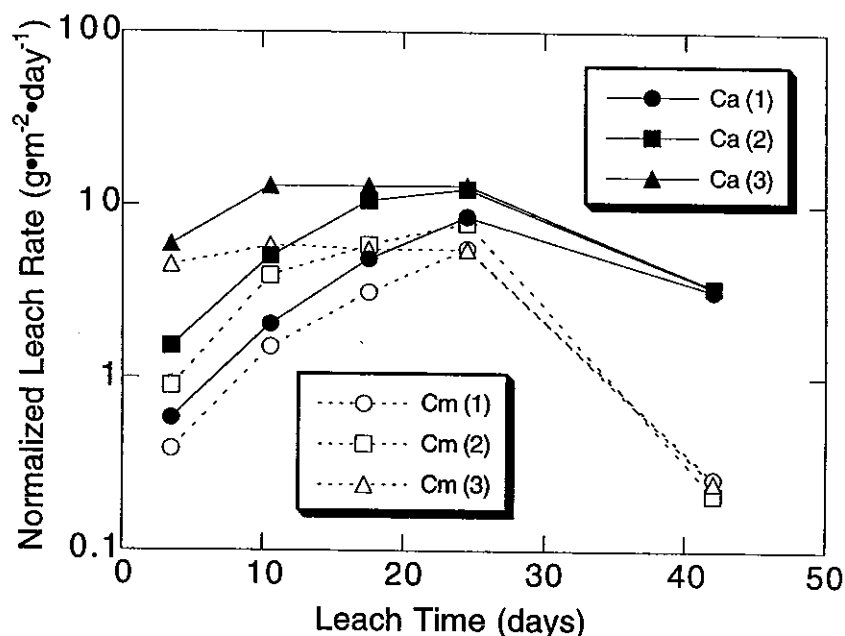


Figure 5.3.4 The normalised leach rate of Cm and Ca from perovskite.

#### 5.4 Fundamental Studies using Natural Analogues of Synroc and Zirconolites

The overall objective of this work is to use natural minerals for insight into the long-term behaviour of individual Synroc phases over geological time. Accordingly, the stability, crystal chemistry, radiation damage effects, and geochemical alteration of natural analogues of Synroc phases, notably zirconolite, have been studied to provide information for long-term modelling of Synroc behaviour in the repository environment. As discussed in Section 4, zirconolite is the phase in Synroc which incorporates most of the tetravalent actinide elements [Lumpkin *et al.*, 1995] and so it becomes of primary importance in revealing the effects of  $\alpha$ -decay damage on the retention of actinides in the waste form over the life of the repository [Hart *et al.*, 1996]. If zirconolite-rich ceramics are used for disposal of weapons-grade Pu, and other actinide waste schemes, radiation damage effects and geochemical alteration are important issues, e.g. Vance *et al.* [1995]. The philosophy of the current research program is to adopt a multidisciplinary approach to problem solving. Currently SEM, TEM, ICP-MS, and  $\alpha$ -spectrometry are employed at ANSTO (collaborations with Dr. R. Gieré (University of Basel, Switzerland) and Dr. C. T. Williams (The Natural History Museum, London) provide expertise and insight into the mineralogy, petrology, and phase chemistry of natural zirconolites).

##### 5.4.1 Zirconolite Occurrence and Conditions of Formation

Comprehensive lists of zirconolite occurrences, host rocks, and associated minerals have been compiled by Williams and Gieré [1996] and Gieré *et al.* [1998b]. These compilations demonstrate that zirconolite crystallises in a wide variety of igneous and metamorphic environments in the Earth's crust and upper mantle, and even in Lunar igneous rock suites. Bulk rock compositions range from ferromagnesian silicate, to alkaline silicate, to magnesium and calcium carbonate-dominated systems. Almost all zirconolite host rocks are silica undersaturated and lack free quartz, suggesting that silica activity plays a major role in the

stability of zirconolite. A few rare exceptions are documented by Harding *et al.* [1982]; De Hoog and Van Bergen [1996].

The data given in **Table 5.4.1** show that zirconolite crystallises at temperatures of 500-1200°C in the Earth's crust and upper mantle [Gieré, 1986; Haggerty 1989; Gieré, 1990; Gieré and Williams, 1992; Harley, 1994]. Estimates of oxygen fugacity (see **Table 5.4.1**) fall between the iron-wüstite and magnetite-hematite buffers (e.g., [Haggerty, 1976]). Host rocks — syenites, metamorphic, and metasomatic rocks crystallised at intermediate silica activities, based on the ubiquitous presence of sphene, and absence of either quartz or perovskite. Carbonatites and kimberlites appear to have crystallised at lower silica activities due to the common occurrence of perovskite and absence of sphene and quartz.

Allen and Ellis [1996] have carried out a theoretical analysis of the stability and phase relations of zirconolite in the system Ca-Si-Ti-Zr-O-C. The analysis suggests that the limited occurrence of zirconolite in nature is largely due to bulk rock composition and not to any inherent restriction in the stability of the mineral itself. In a pure CO<sub>2</sub> fluid, the lower boundary of the thermodynamic stability field of zirconolite is constrained to lie between the lower stability limits of sphene and perovskite, and could extend to temperatures as low as 400°C at very low pressure. Furthermore, the lower limit of zirconolite stability will expand to even lower temperatures in the presence of H<sub>2</sub>O rich fluids and in more complex, multi-component systems.

**TABLE 5.4.1**  
**Conditions of Formation of Zirconolite Host Rocks**

Rock type	Temperature	Pressure	Other parameters
kimberlite	~ 800-1000 °C	< 20-30 kbar	log $f_{O_2}$ < -11 to -10 bar log $a_{SiO_2}$ = low
granulite partial melt	1100-1170 °C	3-4 kbar	log $f_{O_2}$ = unknown log $a_{SiO_2}$ = moderate
syenite	600-900 °C	< 4 kbar	log $f_{O_2}$ = -20 to -14 bar log $a_{SiO_2}$ = -1.7 to -0.3
carbonatite	560-710 °C	< 2 kbar	log $f_{O_2}$ = -24 to -17 bar log $a_{SiO_2}$ < -1.8 to -1.2
metamorphic	≤ 650 °C	≤ 5 kbar	log $f_{O_2}$ = moderate log $a_{SiO_2}$ = moderate
metasomatic	500-600 °C	1-4 kbar	log $f_{O_2}$ = moderate log $a_{SiO_2}$ = moderate XCO <sub>2</sub> = up to ~ 0.2

Sources of data: Haggerty [1976], Purtscheller and Tessardi [1985], Gieré [1986], Gieré [1990], Haggerty [1989], Gieré and Williams [1992], Harley [1994], Pan [1997].

### 5.4.2 Crystal Chemistry of Natural Zirconolite

Composition ranges for major and minor elements in zirconolite are summarised in **Table 5.4.2**. It is clear from this information that the compositions of natural zirconolites are extremely complex and exhibit extensive substitution at the Ti-sites (M5,6) and Ca-site (M8). In terms of atoms per formula unit, the principal cations to substitute for Ti are Nb, Fe, Mg, and Al; whereas, the major elements to substitute for Ca are REEs, Th, and U. The data given in **Table 5.4.2** indicate that the composition of zirconolite reflects that of its host rock [Allen and Ellis, 1996].

**TABLE 5.4.2**  
**Summary of the Chemical Composition of Natural Zirconolite**

		Weight percent oxides			Atoms per formula unit (O = 7)	
		minimum	maximum		minimum	maximum
Ti-sites (M5,6)	WO <sub>3</sub>	0.0	1.5	W	0.00	0.03
	Nb <sub>2</sub> O <sub>5</sub>	0.0	27.0	Nb	0.00	0.65
	Ta <sub>2</sub> O <sub>5</sub>	0.0	5.9	Ta	0.00	0.12
	TiO <sub>2</sub>	13.5	45.9	Ti	0.70	1.97
	Al <sub>2</sub> O <sub>3</sub>	0.0	3.5	Al	0.00	0.26
	MgO	0.0	3.6	Mg	0.00	0.33
	MnO	0.0	2.0	Mn	0.00	0.13
	FeO*	0.7	11.4	Fe*	0.03	0.67
Zr-site (M7)	ZrO <sub>2</sub>	22.8	45.5	Zr	0.72	1.37
	HfO <sub>2</sub>	0.0	1.4	Hf	0.00	0.03
Ca-site (M8)	ThO <sub>2</sub>	0.0	22.3	Th	0.00	0.39
	UO <sub>2</sub>	0.0	24.0	U	0.00	0.38
	REE <sub>2</sub> O <sub>3</sub>	0.0	32.0	REE	0.00	0.88
	CaO	1.8	16.6	Ca	0.13	1.00
	PbO	0.0	2.2	Pb	0.00	0.04
Fe valence	Fe <sub>2</sub> O <sub>3</sub>	1.0	7.7	Fe <sup>3+</sup>	0.05	0.40
	FeO	0.3	6.0	Fe <sup>2+</sup>	0.01	0.35

\* Total Fe content given in the reduced valence state as reported in most electron microbeam analyses. Separate data for Fe valence based on wet chemical analyses. Sources of data: Williams and Gieré [1996], Lumpkin *et al.* [1997], Ewing *et al.* [1982], Oversby and Ringwood [1981], unpublished analyses of G.R. Lumpkin and C.T. Williams.

The major substitution mechanisms described to date for natural zirconolites are listed in **Table 5.4.3**. Previous work on metasomatic zirconolites [Williams and Gieré, 1988; Gieré and Williams, 1992, Lumpkin *et al.*, 1994a] and on zirconolites formed by partial melting in high grade metamorphic rocks [Harley, 1994] provided evidence for major coupled substitutions (1-4) involving REEs, Th, and U. A detailed analysis of the chemistry of natural zirconolite from many localities [Gieré *et al.*, 1998b] has provided evidence for additional coupled substitutions (5-9, 12) and two simple substitutions (10, 11). The available results suggest that, although there are many possible substitution mechanisms, the chemical variation of natural zirconolite is dominated by only a few. These major substitutions are related to the rock-fluid geochemistry and possibly to the oxygen fugacity during crystallisation. Wet chemical analyses summarised in **Table 5.4.2** indicate that natural zirconolites can incorporate large amounts of Fe<sup>2+</sup> and Fe<sup>3+</sup> at the Ti-sites (M5,6), with Fe<sup>2+</sup>/Fe(total) ranging from 0.08 to 0.86.

**TABLE 5.4.3**  
**Potentially Important Chemical Substitutions Identified in Natural Zirconolite**

Substitution	Number
$M8_{Ca} + M5,6Ti \leftrightarrow M8_{REE} + M5,6(Al, Fe^{3+})$	1
$M8_{Ca} + M5,6Ti \leftrightarrow M8(Th, U) + M5,6(Mg, Fe^{2+})$	2
$M8_{Ca} + M5,6Ti_2 \leftrightarrow M8_{REE} + M5,6Fe^{2+} + M5,6(Nb, Ta)$	3
$M8_{Ca_2} + M5,6Ti \leftrightarrow M8_{REE_2} + M5,6(Mg, Fe^{2+})$	4
$M5,6Ti_2 \leftrightarrow M5,6(Nb, Ta) + M5,6(Al, Fe^{3+})$	5
$M8_{Ca} + M5,6Ti_2 \leftrightarrow M8(Th, U) + M5,6(Al, Fe^{3+})_2$	6
$M8_{Ca} + M5,6(Nb, Ta) \leftrightarrow M8(Th, U) + M5,6(Al, Fe^{3+})$	7
$M8_{REE} + M5,6Ti \leftrightarrow M8(Th, U) + M5,6(Al, Fe^{3+})$	8
$M8_{REE} + M5,6Ti \leftrightarrow M8_{Ca} + M5,6(Nb, Ta)$	9
$M5,6Zr \leftrightarrow M5,6Ti$	10
$M7Ti \leftrightarrow M7Zr$	11
$M8_{Ca} + M7Zr \leftrightarrow M8_{REE} + M7_{REE}$	12

Sources of data: Gieré [1986], Williams and Gieré [1988], Gieré and Williams [1992], Harley [1994], Lumpkin *et al.* [1994], Lumpkin *et al.* [1997], Gieré *et al.* [1998b].

The polytypes of zirconolite from three localities have been determined by electron diffraction and are either perfect 2M zirconolite or predominantly 2M with some twinning and stacking disorder [White, 1984]. Two samples are rich in Fe and Nb, indicating that in natural zirconolite the 2M polytype is not restricted to compositions near the CaZrTi<sub>2</sub>O<sub>7</sub> end-member. This has been confirmed by the synthesis of the CaZrNbFeO<sub>7</sub> end-member which exhibits monoclinic 2M symmetry [E.R. Vance and G.R. Lumpkin, unpublished data].

### 5.4.3 Geochemical Alteration of Natural Zirconolite

Oversby and Ringwood [1981] previously demonstrated that zirconolite has remained a closed system to U, Th, and Pb for up to 550 m.y. Extensive searching has revealed evidence for the corrosion, alteration, or replacement of the mineral at only six localities (see Table 5.4.4). The mineralogy and conditions of alteration are reasonably well documented at two of these localities [Gieré, 1990; Gieré and Williams, 1992; Pan, 1997]. In these examples, the corrosion and replacement of zirconolite occurred under unusually extreme conditions at temperatures above 500°C in the presence of a metasomatic or regional metamorphic aqueous fluid phase (Table 5.4.4). In four other cases [Lumpkin *et al.* 1994b; C.T. Williams, unpublished data], the alteration involves increased Si and/or replacement by a silicate mineral phase (Table 5.4.4). These observations point to the instability of zirconolite in the presence of hydrothermal fluids rich in Si; however, zirconolite appears to be highly resistant to aqueous alteration at low temperatures due to kinetic factors.

**TABLE 5.4.4**  
**Examples of the Corrosion, Alteration, or Replacement of Zirconolite**

Locality	Rock type	Description
Adamello, Italy	Metasomatic veins in dolomite marble	Corrosion and replacement of zirconolite by a later generation of zirconolite or betafite. Hydrothermal conditions: 500-600 °C, 1-2 kbar, relatively acidic, reducing fluid phase.
Manitouwadge, Ontario, Canada	Metamorphosed ferromagnesian silicate rocks	Replacement of zirconolite by zircon, sphene, and rutile. Regional metamorphic conditions: 620-680°C, 5-7 kbar, H <sub>2</sub> O rich fluid phase, presence of quartz indicates silica saturation.
Phalaborwa, South Africa	Carbonatite complex	Alteration of zirconolite along microfractures. Incorporation of Si, loss of Ca, Ti, and Fe, hydration, and precipitation of galena. Specific conditions unknown.
Langesundfjord district, Norway	Nepheline syenite	Patchy alteration of zirconolite. Incorporation of Si, loss of Ca and Fe, hydration. Specific conditions unknown.
Sebl-yavr, Kola peninsula, Russia	Carbonatite complex	Replacement of zirconolite by an unidentified Ba, Ti, Nb, Zr silicate phase. Hydration and loss of Ca and Fe. Specific conditions unknown.
Cummins Range, Western Australia	Carbonatite complex	Patchy replacement of zirconolite by an unidentified Ti, Zr, REE silicate phase. Specific conditions unknown.

Sources of data: Gieré and Williams [1992]; Lumpkin *et al.* [1994b]; Pan [1997]; unpublished data of A.N. Mariano, C.T. Williams.

Zirconolite, zircon, and pyrochlore are all highly durable in hydrothermal fluids and commonly survive the complete destruction of their host rocks by weathering, retaining actinides in the process. Pyrochlore has been studied extensively [Lumpkin and Ewing, 1992, 1995; 1996; Lumpkin, 1998] and commonly exhibits alteration in the form of ion exchange and leaching of Na, Ca, and F in low temperature environments. In contrast, perovskite rarely survives the destruction of its host rock by weathering and is usually partially or completely altered to anatase (e.g., Erickson and Blade, 1963; Mariano, 1989). The alteration and replacement of perovskite at elevated temperatures has also been recently documented by Mitchell and Chakmouradian [1998] and Lumpkin *et al.* [1998a].

#### **5.4.4 Radiation Damage**

Previous work has shown that alpha-decay damage causes a crystalline to amorphous transformation in natural zirconolite [Ewing and Headley, 1983; Lumpkin *et al.*, 1986], but an accurate assessment of the dose required to cause the transformation has never been made. Results are now available for samples ranging in age from 16 m.y. to 2 b.y. [Lumpkin *et al.*, 1994b, 1997, 1998b]. For young samples the transformation zone ranges from a dose of  $0.05\text{-}0.1 \times 10^{16}$  to  $1\text{-}2 \times 10^{16}$   $\alpha/\text{mg}$  (0.03-0.08 to 0.8-1.6 dpa). **Figure 5.4.1** shows that the transformation increases as a function of the age of the samples, consistent with a model of long-term annealing of alpha-recoil collision cascades. The calculated annealing rate constant is approximately  $10^{-9}$   $\text{yr}^{-1}$  based on exponential curve fits to the data. Microstructural features of zirconolite are consistent with model of accumulation and overlap of alpha-recoil collision cascades with increasing dose [Lumpkin *et al.*, 1997].

The available data for natural zirconolite indicate that the dose range of the transformation zone is similar to that of natural zircon and pyrochlore [Holland and Gottfried, 1955; Lumpkin and Ewing, 1988; Murakami *et al.*, 1991]. Minor differences in the behaviour of these phases may be related to the fundamental properties of crystal structure and bonding (e.g., Eby *et al.*, 1992; Hobbs *et al.*, 1996; Wang *et al.*, 1997) or to differences in the thermal history. Lumpkin *et al.* [1998b] have suggested that most natural zirconolite host rocks cooled rapidly through 300 °C, followed by slow cooling to near surface conditions. The fact that relatively young natural zirconolites become amorphous at a dose 2-4 times higher than synthetic samples doped with  $^{238}\text{Pu}$  or  $^{244}\text{Cm}$  (e.g., Clinard *et al.*, 1984; Weber *et al.*, 1986) is consistent with the long-term storage of natural samples in the Earth's crust at elevated temperatures.

Overall, the following areas have been identified where further work would be of potential value:

- 1) Detailed studies of the geochemical alteration of natural zirconolite from selected localities would provide valuable insight into its kinetic and thermodynamic stability. This information is pertinent to validating the performance of zirconolite in repository environments.
- 2) Comparative studies of the durability of zirconolite, perovskite, pyrochlore, and other actinide host phases from the same host rocks are also needed in order to evaluate their relative performance.
- 3) An experimental determination of the zirconolite phase relations in the system Ca-Zr-Ti-Si-O-C-H at elevated P and T is necessary to provide some initial constraints on

the stability of the mineral in the Earth's crust. Furthermore, determination of the thermodynamic properties of zirconolite would permit calculation of zirconolite breakdown reactions in P-T-X space.

- 4) Further experimental studies of the durability of synthetic zirconolites containing REEs and actinides should be carried out in hydrothermal fluids approximating those of natural systems. Moreover, the effect of radiation damage on the aqueous durability of zirconolite should be tested at elevated temperatures. If carried out over a range of temperature, these studies would provide valuable insight into the reaction mechanisms and kinetics.
- 5) A determination of the effect of temperature (up to approximately 300°C) on the amorphisation dose and microstructure of actinide doped zirconolite would provide a temperature scale for comparison with the available data for natural samples.

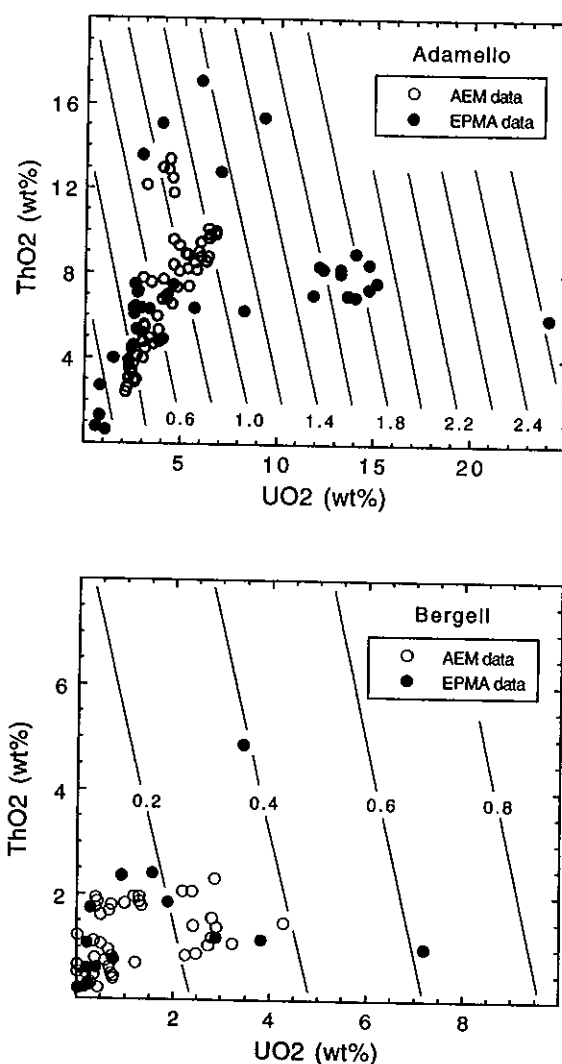


Figure 5.5.2 Plots of the Th and U contents of natural, zoned zirconolites from Adamello, Italy, and Bergell, Switzerland. The plots are contoured for  $\alpha$ -decay dose ( $10^{16}$   $\alpha$ /mg) based on ages of 42 m.y. for Adamello and 31 m.y. for Bergell.

## **6. IMPLICATIONS FOR HLW AND TRU WASTE MANAGEMENT**

### **6.1 Summary of Work Carried out in the Co-operative Program**

The overall aim of the Co-operative Program has been to promote the exchange of information on technology for the management of HLW and to encourage research and development relevant to such technology. During the 13 years that the Program has been carried out, HLW management strategies have matured and developed internationally, and Japan has commenced construction of a domestic reprocessing and vitrification facility for HLW. The HLW management strategy preferred is a national decision. Many countries are using vitrification, direct disposal of spent fuel or a combination of both to handle their existing wastes whereas others have deferred the decision.

In the future, there will be an even more diverse spectrum of high level wastes produced and this diversity will need to be matched by a complementary spectrum of waste forms to provide optimum solutions. The work carried out in the Co-operative program has focussed not only on existing wastes but also on developing technologies that are relevant to new types of HLW, such as those arising from advanced reprocessing and/or partitioning, especially TRU-rich wastes.

The work carried out in the Co-operative Program provides strong scientific evidence that the durability of ceramic waste forms is not significantly affected by radiation damage and that high loadings of actinide elements can be incorporated into specially designed ceramic waste forms. Moreover, natural minerals have been shown to remain as closed systems for U and Th for up to 2.5 b y. All of these results give confidence in the ability of second generation waste forms, such as Synroc, to handle future waste arisings that may not be suitable for vitrification.

Over the life of the Co-operative Program, the preparation of the Cm-doped samples was carried out in JAERI's WASTE-F facility at Tokai with technical input from ANSTO. The results from this work on accelerated radiation damage studies conducted in the specialised facilities in JAERI have contributed strongly to the knowledge on the performance of HLW waste forms over long periods of time. Results from studies of curium-doped Synroc containing simulated JW-A waste showed that leach rates increased as a consequence of the radiation damage, due to (a) microcracking at  $\alpha$ -doses corresponding to  $\geq 10^4$  years of repository storage and (b) atomic displacements within the actinide-bearing phases, zirconolite and perovskite. At high doses, corresponding to  $10^6$  years of storage, the former process led to leach rate enhancements of about a factor of 10 for Na and Cs, whereas the combination of both processes led to leach rates, for Sr and Ca, that were a further order of magnitude higher. Modifications to the Synroc composition were developed at ANSTO to prevent microcracking when the  $\text{Na}_2\text{O}$  content of the Synroc exceeds  $\sim 1.5$  wt%.

Comparative studies were carried out on Synroc-C containing Na-free PW-4b waste and in this case, after  $\sim 10^5$  years of equivalent storage, Sr and Ca leach rates increased by a factor of 10, whereas leach rates of elements not contained in actinide host phases, e.g. Ba and Cs, did not increase with equivalent storage time. These results reflect the absence of microcracking in these specimens. The density decrease due to radiation damage was less in samples stored at  $200^\circ\text{C}$  than at  $30^\circ\text{C}$ .

Complementary studies carried out at ANSTO have further developed this knowledge by focussing on actinide-rich formulations and by extending the confidence in ceramic waste forms from studies of naturally-occurring minerals. These studies have confirmed that zirconolite-rich ceramic formulations can be prepared with good microstructures and very good leaching behaviour. XANES studies of materials have provided data on the valence state of actinide elements in these formulations. Further, studies carried out using natural samples have established that zirconolite remains as a closed system for U and Th over geological periods of time even when the structure has been rendered aperiodic by radiation damage.

In more detail the work carried out in the Co-operative Program has established that;

- Cm-doped reference Synroc containing simulated PW-4b waste prepared in the hot-cell facility at JAERI has the expected phase distribution and physical properties. Leach rates of inactive elements from this material are comparable to those prepared in the open laboratory.
- Samples of reference Synroc with an equivalent storage age of 13,000 years exhibit Ba and Mo leach rates which are similar to those for 'cold' Synroc samples. Leach rates of Cs are most affected by  $\alpha$ -decay damage being a factor of between 5 and 10 higher than that for the 50 year sample. The increase in Ca and Sr leach rates is not as pronounced.
- Cm leach rates from Synroc are unaffected by  $\alpha$ -decay damage, and are instead apparently dictated by the pH of the leachant.
- The density of the Cm-doped reference Synroc decreased linearly with dose and there was no evidence of macro-cracking. Storage of the samples at 200°C reduced the density deficit per unit  $\alpha$ -dose by a factor of 2 compared to that of the sample stored at room temperature.
- Studies of the Np leach rates of Np-doped Synroc made at ANSTO established that the solution leach rate under oxic conditions was a factor of 10 higher than those under anoxic conditions. The presence of Boom clay (geological host material for the Belgian repository concept) did not affect the leaching behaviour of Np under anoxic conditions.
- Initial studies of the kinetics and mechanisms of leaching from Synroc have established that releases are not congruent. Future modelling studies will therefore need to include allowances for the effect of hydrated surface layers.
- Experimental characterisation of incorporation of rare earths and actinides in zirconolite established the preferred substitution mechanisms and confirmed the valence state of substituting cations.
- A new zirconolite-rich Synroc formulation has been shown to exhibit satisfactory leaching performance for Nd and U.
- Studies of naturally-occurring zirconolites have established that these are viable analogues for the zirconolite phase in Synroc. The major projects on the crystal chemistry and radiation damage of zirconolite have been completed. However, additional work on: mineralogy, petrology, and geochemistry of zirconolite-bearing rocks with emphasis on P-T-X conditions under which the phase has survived would be valuable. Moreover determination of the stable and radiogenic isotope systematics of altered zirconolites; durability studies of zirconolite; determination of annealing kinetics

of radiation-damaged zirconolite and experimental studies of the effect of radiation damage on the dissolution of natural zirconolite would also be of value.

## **6.2 Conclusions**

The Co-operative Program has been very successful. It has confirmed the viability of Synroc as a means of dealing with both reference HLW and Japanese HLW and TRU-rich waste streams.

The program has clearly established that the ceramic waste forms studied in the Program are mature. This has been demonstrated not only in laboratory studies using accelerated leaching and radiation damage studies but also by use of appropriate natural analogue samples to allow the description of some performance data over geological time.

The Co-operative Program has enhanced the excellent co-operative working relationship between the two institutions, and the arrangements developed under the original agreement should serve as a model for any other co-operative projects developed in the future.

## APPENDIX 1

### SCOPE OF RESPONSIBILITIES OF THE LEAD INSTITUTIONS

The Implementing Arrangements defined the General Scope of Responsibilities of the co-operation in each phase of the collaboration, as follows.

#### **PHASE I STUDY** (for a period of five (5) years from September 3, 1985)

ANSTO and JAERI will co-operate in studies on SYNROC as a waste form to evaluate the SYNROC system for the management of high level radioactive wastes.

#### JAERI responsibilities

JAERI will prepare samples of SYNROC containing alpha radioactive nuclides and real wastes on the basis of hot cell techniques accumulated in JAERI and upon information provided by AAEC.

JAERI will evaluate the performance and capability of SYNROC as a waste form for high level radioactive waste.

JAERI will develop fabrication apparatus appropriate for operation of hot cells and prepare SYNROC specimens containing real wastes and will study alternative fabrication procedures of SYNROC.

JAERI will conduct irradiation tests of SYNROC specimens containing non-radioactive simulated wastes and examine characteristics of SYNROC specimens containing actinide nuclides and those containing real wastes.

JAERI will collaborate in evaluating capability and feasibility of the SYNROC system in the high level waste management based on the results obtained through the co-operative studies described in this Appendix.

#### AAEC responsibilities

AAEC will provide information on laboratory scale SYNROC fabrication process to JAERI to allow JAERI to undertake JAERI's responsibilities.

AAEC, in collaboration with the Australian National University, will continue established research programs on the formulation and fabrication of SYNROC and will continue with research on the incorporation of some radioactive nuclides to small SYNROC samples.

AAEC will study fabrication procedures of SYNROC under various conditions to obtain data necessary for hot cell fabrication.

AAEC will examine characteristics of SYNROC specimens.

**PHASE II STUDY** (initially for a period of five (5) years from September 3, 1990 but then extended to September 3, 1998)

ANSTO and JAERI will co-operate in studies on SYNROC for a period of another five (5) years from September 3, 1990 according to the following scope of responsibilities.

JAERI responsibilities

JAERI will continue alpha acceleration test for standard SYNROC and evaluate the performance and capability of SYNROC as a waste form for high-level radioactive wastes.

JAERI will prepare samples of SYNROC containing TRU elements on the basis of hot cell techniques accumulated in JAERI and upon information provided by ANSTO.

JAERI will conduct fundamental research on TRU immobilisation mechanism and study the matrix stability of SYNROC by long-term durability test under the collaboration between ANSTO and JAERI.

JAERI will collaborate in evaluating capability and feasibility of SYNROC system in the high-level waste and TRU waste management based on the results obtained through the co-operative studies described in this Appendix.

ANSTO responsibilities

ANSTO will continue to assess the radiation performance of SYNROC by studies which will include neutron irradiation and natural mineral analogues, and will cooperate with JAERI in the continued evaluation of alpha stability tests.

ANSTO, in collaboration with the Australian National University, will study the formulation, testing and optimisation of SYNROC for immobilisation of TRU elements from the perspectives of waste partitioning, FBR wastes, higher burnup LWR fuel, and other TRU streams.

ANSTO will conduct fundamental research on TRU immobilisation mechanisms, including matrix stability, by structural, leaching and geochemical modeling studies involving SYNROC containing simulated wastes and actinides.

ANSTO will collaborate in evaluating capability and feasibility of the SYNROC system in the high-level waste and TRU waste management based on the results obtained through the cooperative studies described in this Appendix.

**APPENDIX 2**

**MEETINGS OF CO-ORDINATION AND STEERING COMMITTEES**

A. Co-ordination Committee Meetings

Meeting No.	Date	Location	Chairman
1	July 19, 1984	Tokyo	M. Nakamura
2	November 24, 1984	Canberra	B. Hill
3	September 3, 1985	Tokyo	T. Matsui
4	November 25, 1986	Canberra	W. M <sup>c</sup> Gregor
5	April 11, 1988	Tokyo	A. Yuki
6	January 29, 1990	Canberra	R. Rawson
7	November 22, 1991	Tokyo	H. Ishida
8	November 4, 1992	Canberra	R. Rawson
9	November 3, 1994	Tokyo	T. Kuramochi
10	June 14, 1996	Canberra	R. Rawson
11	August 21, 1998	Tokyo	S. Aoyama

B. Steering Committee meetings

Number: 1 Date: September 4, 1985 Location: Tokai  
Participants: JAERI T. Fuketa  
K. Imai  
H. Umezawa  
ANSTO D. Walker  
A. Jostsons  
ANU A. Ringwood

Number: 2 Date: March 14, 1986 Location: Lucas Heights  
Participants: ANSTO P. Kelly  
A. Jostsons  
ANU A. Ringwood  
JAERI K. Imai  
H. Umezawa.  
H. Nakamura

Number: 3 Date: September 8, 1986 Location: Tokai  
Participants: JAERI T. Fuketa  
K.. Araki  
ANSTO P. Kelly  
A. Jostsons

Number: 4 Date: April 14, 1987 Location: Lucas Heights  
Participants: ANSTO - P. Kelly (Chairman)  
A. Jostsons  
ANU - A. Ringwood  
JAERI - K. Iwamoto, S. Tashiro  
S. Sekine

Number: 5 Date: September 16, 1987 Location: Tokai  
Participants: JAERI - T. Asaoka (Chairman)  
K. Hirano, S. Tashiro  
ANSTO - A. Jostsons, C. Hardy

Number: 6 Date: April 8, 1988 Location: Tokai  
Participants: JAERI - T. Asaoka (Chairman)  
K. Hirano, S. Tashiro  
ANSTO - P. Kelly, A. Jostsons  
ANU - A. Ringwood

Number: 7 Date: November 29, 1988 Location: Lucas Heights  
Participants: ANSTO - A. Jostsons (Chairman)  
K. Reeve  
ANU - A. Ringwood  
JAERI - S. Tashiro

Number: 8 Date: June 27, 1989 Location: Tokai  
Participants: JAERI - H. Hirano (Chairman)  
S. Muraoka  
ANSTO - A. Jostsons  
ANU - A. Ringwood

Number: 9 Date: January 30, 1990 Location: Lucas Heights  
Participants: ANSTO - D. Davy (Chairman)  
A. Jostsons  
ANU - A. Ringwood  
JAERI - S. Taniguchi, Y. Wadachi  
H. Katsuta

Number: 10 Date: August 14, 1990 Location: Tokai  
Participants: JAERI - M. Ichikawa (Chairman)  
S. Matsuura  
S. Muraoka  
ANSTO - A. Jostsons  
E. Vance  
K. Hart

Number: 11 Date: November 22, 1990 Location: Lucas Heights  
Participants: JAERI M. Ichikawa  
S. Muraoka  
ANSTO A. Jostsons  
E. Vance  
R. Hutchings

Number: 12 Date: April 19, 1991 Location: Tokai  
Participants: JAERI S. Matsuura  
M. Ichikawa  
S. Muraoka  
ANSTO A. Jostsons  
ANU A. Ringwood

Number: 13 Date: November 1, 1991 Location: Lucas Heights  
Participants: JAERI M. Ichikawa  
S. Muraoka  
ANSTO A. Jostsons  
E. Vance  
R. Hutchings  
ANU S. Kesson

Number: 14 Date: April 30, 1992 Location: Tokai  
Participants: JAERI M. Ichikawa  
Y. Wadachi  
S. Muraoka  
ANSTO A. Jostsons  
E. Vance  
K. Hart

Number: 15 Date: November 3, 1992 Location: Lucas Heights  
Participants: JAERI M. Ichikawa  
Y. Kishida  
S. Muraoka  
ANSTO H. Garnett  
A. Jostsons  
E. Vance

Number: 16 Date: June 11, 1993 Location: Tokai  
Participants: JAERI M. Ichikawa  
Y. Kishida  
S. Muraoka  
ANSTO H. Garnett  
A. Jostsons  
E. Vance

Number: 17 Date: November 18, 1993 Location: Lucas Heights  
Participants: JAERI M. Ichikawa  
S. Muraoka  
ANSTO H. Garnett  
A. Jostsons  
E. Vance  
ANU S. Kesson

Number: 18 Date: May 9, 1994 Location: Lucas Heights  
Participants: JAERI S. Muraoka  
T. Banba  
ANSTO H. Garnett  
A. Jostsons  
ANU S. Kesson

Number: 19 Date: November 1, 1994 Location: Tokyo  
Participants: JAERI T. Tsujino  
S. Muraoka  
T. Banba  
ANSTO H. Garnett  
A. Jostsons  
ANU S. Kesson

Number: 20 Date: April 28, 1995 Location: Sydney  
Participants: JAERI S. Muraoka  
T. Banba  
ANSTO A. Jostsons  
E. Vance  
ANU S. Kesson

Number: 21 Date: December 13, 1995 Location: Lucas Heights  
Participants: JAERI Y. Kawakami  
T. Banba  
ANSTO H. Garnett  
R. Hutchings  
ANU S. Kesson

Number: 22 Date: June 17, 1996 Location: Lucas Heights  
Participants: JAERI S. Muraoka  
T. Banba  
ANSTO H. Garnett  
A. Jostsons  
ANU S. Kesson

Number:	23	Date:	October 28, 1996	Location:	Tokyo
Participants:	JAERI	Y. Kawakami			
		S. Muraoka			
		T. Banba			
	ANSTO	H. Garnett			
		E. Vance			
	ANU	S. Kesson			
Number:	24	Date:	June 26, 1997	Location:	Lucas Heights
Participants:	JAERI	S. Muraoka			
		T. Banba			
	ANSTO	A. Jostsons			
		E. Vance			
	ANU	S. Kesson			
Number:	25	Date:	August 20, 1998	Location:	Tokyo
Participants:	JAERI	Y. Kawakami			
		S. Muraoka			
		T. Banba			
	ANSTO	P. Duerden			
		K. Hart			
	ANU	S. Kesson			



**APPENDIX 3  
PERSONNEL EXCHANGES**

Name: T. Murakami      From: JAERI      Visited: ANSTO and ANU  
Date: October 1984      Duration: Two weeks  
Purpose: For detailed discussions on SYNROC science and technology, including fabrication methods already developed and used by ANSTO.

Name: W. Buykx      From: ANSTO      Visited: JAERI, Tokai  
Date: Nov/Dec 1987      Duration: Three weeks  
Purpose: To participate in the fabrication of the first set of  $^{244}\text{Cm}$  doped SYNROC samples for accelerated radiation damage testing.

Name: S. Matsumoto      From: JAERI      Visited: ANSTO  
Date: Mar/April 1988      Duration: Three weeks  
Purpose: To participate in the non-radioactive SYNROC fabrication program at ANSTO.

Name: T. Sagawa      From: JAERI      Visited: ANSTO  
Date: Mar/April 1989      Duration: Three weeks  
Purpose: To participate in the assessment of actinide homogeneity in active SYNROC samples by the alpha track etch technique.

Name: E. Vance      From: ANSTO      Visited: JAERI, Tokai  
Date: April 1989      Duration: One week  
Purpose: For detailed discussions on the radiation damage testing of SYNROC by actinide doping.

Name: K. Hart      From: ANSTO      Visited: JAERI, Tokai  
Date: May 1989      Duration: 1 week  
Purpose: To participate in joint experimental studies on the leaching of SYNROC doped with  $^{244}\text{Cm}$ .

Name: M. Stewart      From: ANSTO      Visited: JAERI, Tokai  
Date: Mar/April 1990      Duration: Three weeks  
Purpose: To participate in the fabrication of the second set of  $^{244}\text{Cm}$  doped SYNROC samples (containing sodium-free PW-4b simulated waste) for accelerated radiation damage testing.

Name: Y. Togashi      From: JAERI      Visited: ANSTO  
Date: May/June 1990      Duration: Three weeks  
Purpose: To participate in an investigation into the effect of leachant composition on the release of plutonium from SYNROC.

Name: Y. Tamura      From: JAERI      Visited: ANSTO, Lucas Heights  
Date: November 1991      Duration: Three weeks  
Purpose: Liquid analyses and radioanalyses on leachate samples from Synroc.

Name: K. Hart                      From: ANSTO                      Visited: JAERI, Tokai  
Date: April 1992                      Duration: Ten days  
Purpose: Preparation of joint publications arising from the co-operative program.

Name: E. Vance                      From: ANSTO                      Visited: JAERI, Tokai  
Date: April 1992                      Duration: Ten days  
Purpose: Preparation of joint publications arising from the co-operative program.

Name: T. Tsuboi                      From: JAERI                      Visited: ANSTO, Lucas Heights  
Date: November 1992                      Duration: Three weeks  
Purpose: Study of the use of XRD technique for the examination of Synroc specimens.

Name: B. Begg                      From: ANSTO                      Visited: JAERI, Tokai  
Date: February 1993                      Duration: Three weeks  
Purpose: Preparation and characterisation of zirconolite samples.

Name: K. Hart                      From: ANSTO                      Visited: JAERI, Tokai  
Date: April 1993                      Duration: One week  
Purpose: Preparation of joint publications and scientific discussions on the collaboration.

Name: E. Vance                      From: ANSTO                      Visited: JAERI, Tokai  
Date: April 1993                      Duration: One week  
Purpose: Preparation of joint publications and scientific discussions on the collaboration.

Name: S. Kikkawa                      From: JAERI                      Visited: ANSTO, Lucas Heights  
Date: November 1993                      Duration: Three weeks  
Purpose: Study of the fabrication, examination and leaching techniques used at ANSTO for the preparation and characterisation of Synroc.

Name: P. McGlenn                      From: ANSTO                      Visited: JAERI, Tokai  
Date: May 1994                      Duration: One week  
Purpose: Study of the leaching of curium-doped perovskite in the hot-cell facilities at JAERI.

Name: K. Hart                      From: ANSTO                      Visited: JAERI, Tokai  
Date: April 1994                      Duration: One week  
Purpose: Discussions on the scientific progress of the collaboration and to initiate the preparation of the phase II report.

Name: M. Numata                      From: JAERI                      Visited: ANSTO, Lucas Heights  
Date: February 6, 1995                      Duration: Three weeks  
Purpose: Study of the fabrication, examination and leaching techniques used at ANSTO for the preparation and characterisation of actual-sized Synroc.

Name: K. Hart                      From: ANSTO                      Visited: JAERI, Tokai  
Date: 1996                      Duration: 1 week  
Purpose: Discussions on the scientific progress of the collaboration.

Name: K. Hart                      From: ANSTO                      Visited: JAERI, Tokai  
Date: 1997                              Duration: 1 week  
Purpose: Discussions on the scientific progress of the collaboration.



## APPENDIX 4

### WORKSHOPS HELD, DATES, LOCATION AND TOPICS

#### Workshop No. 1

Held at ANSTO, Lucas Heights, Australia on 26-27th November 1986

Participants: A. Yuki	STA, Japan
T. Fuketa	JAERI, Japan
K. Iwamoto	JAERI, Japan
H. Nakamura	JAERI, Japan
H. Kamiyama	JAERI, Japan
K. Ishiguro	PNC, Japan
W. Suginoara	PNC Exp., Australia
K. Hirose	Japanese Embassy
D. Walker	ANSTO, Australia
A. Jostsons	ANSTO, Australia
K. Reeve	ANSTO, Australia
E. Ramm	ANSTO, Australia
D. Levins	ANSTO, Australia
A. Ringwood	ANU, Australia

The main developments reported by JAERI were:

- (i) The excellent very low leachability of SYNROC made at JAERI by methods very similar to those recommended by ANSTO during previous discussions and information exchange. It was also noted that SYNROC samples prepared by each group had been exchanged and characterised as excellent SYNROC.
- (ii) A new procedure developed by JAERI for SYNROC calcination using titanium hydride in place of a reducing gas containing hydrogen.
- (iii) Results on the irradiation of SYNROC using charged particles.
- (iv) Progress in the commissioning of the In-cell Solidification Apparatus which was designed and assembled for the fabrication of curium doped SYNROC for accelerated radiation damage experiments. This is a more direct method of studying radiation damage than the charged particle method in use at JAERI or the fast neutron irradiation method used by ANSTO. In particular it was noted that the setting up of the apparatus in-cell had commenced earlier that month (November 1986).

The main developments reported by ANSTO were:

- (i) The effects of fabrication process and leach testing variables on the leach rates of SYNROC containing simulated non-radioactive waste. These variables included hot pressing conditions, waste loading, impurities, leaching temperature, leaching time, leachant pH and composition, flow rate and solubility effects.
- (ii) Results from ANSTO's fast neutron irradiation program to study radiation damage in SYNROC.

- (iii) Leaching studies on small radioactive samples made at ANSTO containing additions of either transuranic actinides or fission products.
- (iv) The current status of the SYNROC Demonstration Plant.

## **Workshop No. 2**

Held at ANSTO, Lucas Heights, Australia on 13th April 1987.

Participants: K. Iwamoto	JAERI, Japan
S. Tashiro	JAERI, Japan
K. Sekine	JAERI, Japan
H. Mitamura	JAERI, Japan
M. Yamakawa	PNC, Japan
H. Suginoara	PNC Exp., Australia
J. Marples	UKAEA, UK
P. Gerontopoulos	ENEA, Italy
D. Walker	ANSTO, Australia
A. Jostsons	ANSTO, Australia
K. Reeve	ANSTO, Australia
D. Levins	ANSTO, Australia
E. Ramm	ANSTO, Australia
A. Ringwood	ANU, Australia
S. Kesson	ANU, Australia

This workshop was held on the occasion of a meeting of the IAEA Working Group on Radioactive Waste Solidification in Sydney. Representatives from the UKAEA (Harwell) in the UK and the ENEA in Italy, who were attending the IAEA meeting, were invited to attend the workshop. The workshop commenced with an overview of present programs, achievements, and future plans for work on SYNROC being carried out at JAERI, ANSTO/ANU, UKAEA and ENEA. This was followed in the afternoon by an open forum session in which an opening presentation on each of four topics was followed by other presentations and informal discussions. The topics covered were:

Precursors and preparation chemistry (Leader Dr S E Kesson),

Large-scale and active fabrication (Leader Dr K D Reeve),

Chemical durability (Leader Dr D M Levins), and

Disposal concepts (Leader Prof A E Ringwood).

### **Workshop No. 3**

Held at ANSTO, Lucas Heights, Australia on 14-15th November 1989

Participants: Y. Wadachi	JAERI, Japan
H. Mitamura	JAERI, Japan
A. Jostsons	ANSTO, Australia
K. Reeve	ANSTO, Australia
D. Levins	ANSTO, Australia
K. Hart	ANSTO, Australia
E. Vance	ANSTO, Australia
A. Ridal	ANSTO, Australia

The main topics discussed at this workshop were:

- (i) The latest results from JAERI's accelerated radiation damage program based on curium doped SYNROC.
- (ii) ANSTO's results on improving the ability of standard and modified SYNROC compositions to accommodate the significant levels of sodium present in JW-A wastes.
- (iii) Recent leach test results on SYNROC, including SYNROC containing transuranic actinides.
- (iv) The development of waste partitioning methods at JAERI.
- (v) Recent processing developments in ANSTO's SYNROC Demonstration Plant.
- (vi) JAERI work on radionuclide migration testing of the aerated soil layer of a candidate disposal site.

Like its predecessors, this workshop was most successful and further reinforced the excellent collaboration and information exchange between the participants in the co-operative program.

### **Workshop No. 4**

Held at JAERI, Tokai, Japan on 13th August 1990

Participants: A. Jostsons	ANSTO, Australia
K. Hart	ANSTO, Australia
E. Vance	ANSTO, Australia
M. Ichikawa	JAERI, Japan
Y. Wadachi	JAERI, Japan
S. Muraoka	JAERI, Japan
H. Mitamura	JAERI, Japan
S. Matsumoto	JAERI, Japan
Y. Togashi	JAERI, Japan

The main topics discussed at this workshop were:

- (i) Review of Current Status of SYNROC and Future Direction
- (ii) JAERI Work on Cm-doped, Na-bearing SYNROC

- (iii) ANSTO Work on Sodium Containing Non-Radioactive SYNROC
- (iv) Studies of Mechanisms of Inactive SYNROC Leaching
- (v) JAERI Work on Cm-doped, Na-Free Reference SYNROC
- (vi) Preliminary Results on Zirconolite Based Formulation of SYNROC for TRU (Actinide) Waste Immobilisation
- (vii) Review of Recent Actinide Leaching Studies of SYNROC
- (viii) JAERI Work on Glass Waste Forms

This workshop gave a valuable opportunity for the participants to exchange recent experimental results generated within the co-operative program.

### **Workshop 5**

Held at JAERI, Tokai, Japan on October 31, 1994

Participants:

E. Vance	ANSTO, Australia
K. Hart	ANSTO, Australia
K. Smith	ANSTO, Australia
P. McGlenn	ANSTO, Australia
S. Kesson	ANU, Australia
T. Banba	JAERI, Japan
H. Kamizono	JAERI, Japan
T. Muromura	JAERI, Japan
Y. Morita	JAERI, Japan
H. Mitamura	JAERI, Japan
K. Kuramoto	JAERI, Japan

The main topics discussed at this workshop were;

1. Research and development of HLW partitioning
2. Update on current research on Synroc being carried out at ANSTO
3. New ceramic waste form for disposition of plutonium
4. Natural analogue studies being undertaken within the Synroc program
5. Durability of  $\text{La}_2\text{Zr}_2\text{O}_7$  waste form
6. Development of secondary phases on Synroc leached at  $150^\circ\text{C}$
7. Durability of YSZ- $\text{Al}_2\text{O}_3$  composite ceramic waste form
8. The effect of pH on the leaching of zirconolite and perovskite
9.  $\alpha$ -decay damage of actinide-host phases

## **Workshop 6**

Held at JAERI, Tokai, Japan on November 4, 1997

Participants:	K. Hart	ANSTO, Australia
	P. M <sup>c</sup> Glenn	ANSTO, Australia
	S. Kesson	ANU, Australia
	M. Kubota	JAERI, Japan
	T. Ohnukio	JAERI, Japan
	T. Ogawa	JAERI, Japan
	Y. Morita	JAERI, Japan
	H. Mitamura	JAERI, Japan
	T. Yamaguchi	JAERI, Japan
	K. Kuramoto	JAERI, Japan

At this workshop the OMEGA program, Synroc developments, sorption studies on back fill materials, ceramic waste forms, transmutation fuels and natural analogue work were discussed.



## APPENDIX 5

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**APPENDIX 6**

**REPORTS AND PUBLICATIONS RESULTING FROM THE  
JAERI/ANSTO CO-OPERATIVE PROGRAM ON SYNROC**

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