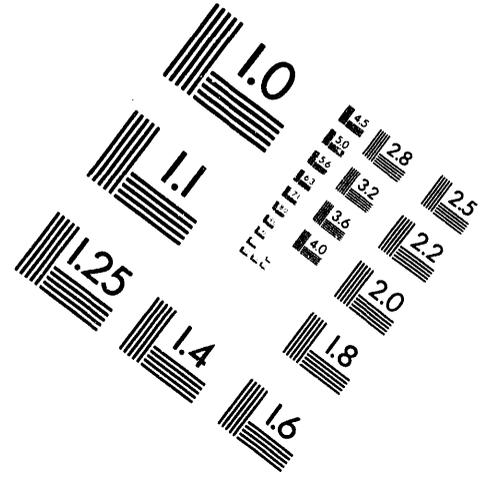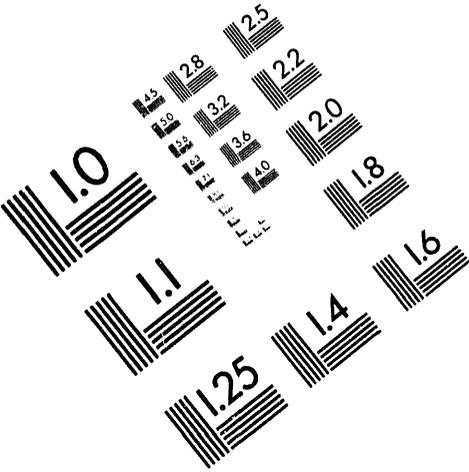# AIIM

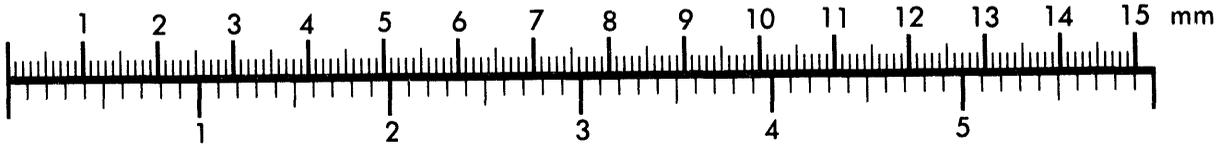**Association for Information and Image Management**

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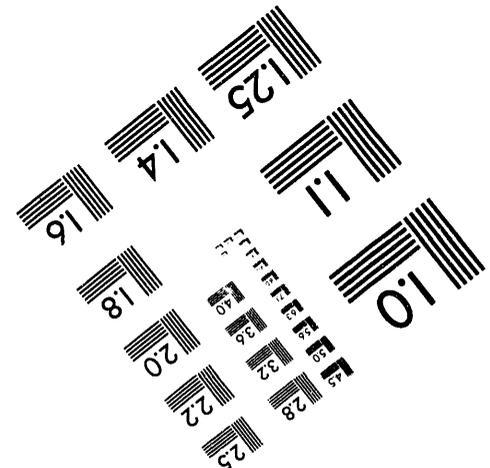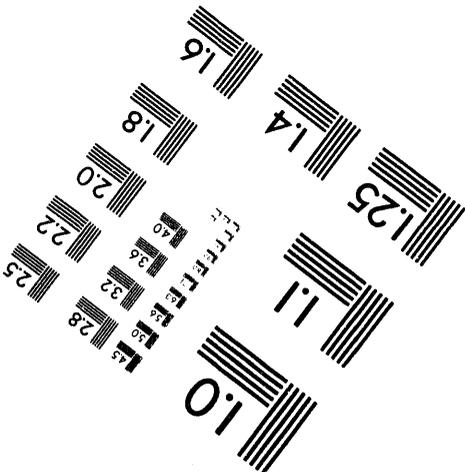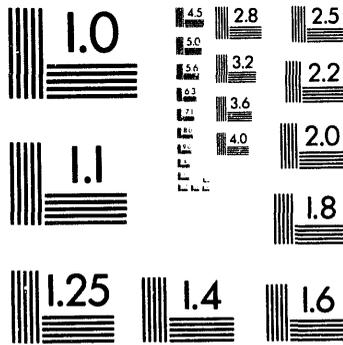
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Ceramic Waste Forms for Fuel-Containing Masses at Chernobyl

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May 1994

Lawrence Livermore National Laboratory

MASTER

DISCLAMER

CERAMIC WASTE FORMS FOR FUEL-CONTAINING
MASSES AT CHERNOBYL

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ABSTRACT

The fuel materials originally in the core of the Chernobyl Unit 4 reactor are now present within the Ukrytie in three major forms: (1) very fine particles of fuel dispersed as dust (about 10 tonnes), (2) fragments of the destroyed core, and (3) lavas containing fuel, cladding, and other materials. All of these materials will need to be immobilized into waste forms suitable for final disposal. We propose a ceramic waste form system that could accommodate all three waste types with a single set of processing equipment. The waste form would include the mineral zirconolite for immobilization of actinide materials (including uranium), perovskite, nepheline, spinel, and other phases as dictated by the chemistry of the lava masses. Waste loadings as high as 50% U can be achieved if pyrochlore, a close relative of zirconolite, is used as the U host. The ceramic immobilization could be achieved with low additions of inert chemicals to minimize the final disposal volume while ensuring a durable product. The sequence of processing would be to collect and immobilize the fuel dust first. This material will require minimal preprocessing and will provide experience in the handling of the fuel materials. Core fragments would be processed next, using a cryogenic crushing stage to reduce the size prior to adding ceramic additives. The lavas would be processed last, which is compatible with the likely sequence of availability of materials and with the complexity of the operations. The lavas will require more adjustment of chemical additive composition than the other streams to ensure that the desired phases are produced in the waste form.

I. INTRODUCTION

The reactor in Unit 4 at Chernobyl, Ukraine, was destroyed in an explosive accident in 1986. The accident resulted in debris being thrown out of the reactor building and into the surroundings of the reactor site, as well as fine particle size debris reaching the upper atmosphere and being carried to distant locations. Radioactive contamination carried in the lower parts of the atmosphere was washed out by rain and was predominantly deposited in Byelorussia.[1]

Immediately following the accident an emergency clean-up effort was started. As part of the attempts to contain the radioactive debris within a limited location, a sarcophagus or Shelter (Ukrytie) was built around the destroyed reactor area. The structure used the remains of the reactor building as part of its structural support and added concrete walls and metal roofing materials. The difficulties caused by the damaged site and building and by the high radiation levels made sealing of the building difficult and inspection of the work impossible.[2] Cracks in the walls and the roof could not be sealed, meaning that the interior of the sarcophagus was exposed to the weather. On the north side of the building a cascade wall was built in the form of steps several meters in width and height, within which containers of radioactive waste and damaged metal were sealed.[2]

Because the sarcophagus building was known to contain major defects and to be deteriorating with time, the Ukrainian government initiated an international competition to design a replacement structure that would provide more stable and secure isolation of the damaged and contaminated areas of the reactor. As background information for that competition, much information about the state of the reactor and the fuel-containing debris was made available.[3] A group of scientists and engineers at Lawrence Livermore National Laboratory participated in a consortium led by the Oxford (England) School of Architecture Extreme Environments Laboratory that resulted in a design concept called "Pprotector", which stands for Protective Pyramid and Robotic Technologies for Ecological Transformation of Reactor. As part of the competition input, we developed a system of waste form

materials based on titanate ceramics to immobilize the radioactive materials presently dispersed within the existing Ukrytie and surrounding areas. In this paper, I will review the present condition of the fuel containing materials at the Chenobyl Unit 4 site, the suite of titanate ceramic waste forms that might be used to cover the range of waste types, and the sequence of operations that could be used in the clean-up and immobilization effort.

II. DESCRIPTION OF FUEL-CONTAINING MATERIALS

The original content of the reactor core was exploded out of the reactor and now exists in three main forms:

A. Core fragments that were ejected into the upper levels of the reactor building and later collected and thrown back into the reactor. Some fuel fragments were thrown onto the roof of the building, including the central room, while others were ejected outside the building and are now buried under the cascade wall.[3]

B. Fuel dust and hot particles ranging in size from fractions of a micrometer to hundreds of micrometers are distributed inside the sarcophagus. The dust particles have penetrated the walls, floors, and ceilings of rooms and are readily dispered into the air. The estimated amount of fuel present as dust is 10 tonnes.[2]

C. Much of the core became molten and mixed with other materials as it "ate" its way out of the reactor vessel and through walls and floors of the building. The lava materials have the following range of chemistry[3]

UO_2	up to 18%
K_2O	1 to 2 %
CaO	4 to 10 %
MgO	3 to 7 %
Al_2O_3	2 to 12%
Fe_2O_3	3 to 10%
ZrO_2	2 to 4%
SiO_2	up to 60%

As can be seen from the ranges of concentration given above, the waste form for the lava masses will need to be very flexible with respect to waste stream composition.

III. TITANATE CERAMIC WASTE FORMS

In the late 1970s and early 1980s, Prof. A. E. Ringwood proposed and developed a waste form for immobilization of the fission product and actinide residues resulting from reprocessing of spent fuel from commercial nuclear power reactors.[4] The waste form, Synroc C, consisted of three minerals to accommodate the majority of the radioactive species, a metal phase that contained the

noble metal fission products and technetium, and rutile that was used as a compositional buffer. The minerals that incorporated the main fission products and actinides were barium hollandite to incorporate Cs, perovskite to immobilize Sr and some of the actinides, and zirconolite, which can incorporate a wide range of chemical variations including REE and actinides. Waste loadings of 20% fission products and actinides were demonstrated to be achievable using surrogate materials to simulate the waste.[5] The ceramic was formed into monoliths by pressing in a stainless steel bellows using uniaxial pressure applied at temperatures of 1100 to 1150°C. A few percent of Ti metal was added to the mixture of ceramic former and waste before putting into the bellows. This accompiished two things: first, it acted as a getter for any oxygen sorbed on the powder surfaces; second, it ensured that the redox conditions in the ceramic would be buffered by the Ti^{3+}/Ti^{4+} couple. The chemistry of the Synroc C waste form was dominated by the chemistry of the host phases and was highly predictable because of the near absence of processing chemicals in the waste stream.

In a parallel effort, Ringwood and workers at Lawrence Livermore National Laboratory developed a titanate-based ceramic waste form tailored to the wastes held in storage tanks at Savannah River. In this case, the wastes contained a large amount of processing chemicals and dissolved cladding and, in the early stages, were to contain substantial amounts of silica through the use of ion exchange resins to remove cesium from the liquid in the tanks.[6] The Ba-hollandite phase used in Synroc C to immobilize Cs is not stable in a mixture containing substantial Si. Consequently, the Synroc D formulation for Savannah River wastes was designed using nepheline, a sodium aluminosilicate, as the Cs host. Since aluminum was abundant in the sludges because it came from the cladding material, this produced a high waste loading for the waste form because the waste elements were used instead of adding process chemicals. The composition of the composite Savannah river sludge plus ion exchange media (loaded with cesium) was[6]

Fe_2O_3	36.13
Al_2O_3	28.26
MnO_2	9.94
U_3O_8	3.26
CaO	2.69
NiO	4.47
SiO_2	0.85
Na_2O	5.08
Na_2SO_4	0.93
Ion-Siv IE-95	8.93

The radioactive species, other than U, contributed a very small amount to the bulk chemistry. This material could be converted into a Synroc D material having four main phases - nepheline, perovskite, zirconolite, and spinel - and a combined waste loading of 70% sludge plus ion

exchange media. The redox state of the waste form was controlled by the Fe^{2+}/Fe^{3+} buffer, which occurred naturally in the waste sludges. The proportions of mineral phases were 18% nepheline, 48% spinel, 19% zirconolite, and 15% perovskite. The ceramic material was to be produced using hot isostatic pressing rather than uniaxial pressing in bellows.[6]

Recently, workers at LLNL have designed a titanate ceramic waste form to immobilize the residues from processing of mixed wastes.[7] These wastes have relatively low radioactivity, but contain a wide variety of chemical elements that require immobilization so that the waste form will be acceptable for disposal as non-hazardous. One of the waste streams considered as part of the mixed waste residue immobilization task was that arising from the processing of mixtures of paper products, plastics, and other materials with high ash content. These materials yielded an average ash content of 10% and a chemical composition (major components only) in wt% of

Al_2O_3	20
CaO	5.3
Fe_2O_3	3.2
K_2O	2
MgO	15
P_2O_5	4.4
SiO_2	34
TiO_2	2.2
ZnO	7.5

The waste form for this material was designed to have 50% loading of this composition and to produce a phase assemblage of zirconolite, perovskite, spinel, and nepheline. The spinel compositions for this waste are, of course, quite different from that produced from the Fe-rich Savannah River wastes. To ensure a low cost and flexible operation in handling the residues, we chose to use oxidizing conditions for the processing and an air sintering of small cold-pressed pellets for the densification step and phase growth step. Processing of 1 cm diameter pellets at 1200°C gave theoretical density in the finished product of about 95%.[7] The composition of the finished waste form for this residue chemistry at 50% loading was

Al_2O_3	40.2
CaO	4.4
Fe_2O_3	1.6
K_2O	1.0
MgO	7.4
Na_2O	7.9
P_2O_5	2.2
SiO_2	16.8
TiO_2	8.9
ZnO	3.7
ZrO_2	3.9

Other	2.0

This chemistry produced a phase assemblage without perovskite because the Ca level was insufficient. We, therefore, decided in future trials to use a waste loading of 45% and increase the Ca by chemical addition. The phase assemblage achieved was 40% nepheline, 40% spinel, 11% zirconolite, and 9 percent of rutile + Ca-phosphate.[7]

IV. DESIGN OF THE WASTE FORM FOR CHERNOBYL

Examination of the chemical composition of the Chernobyl lavas suggested that a waste form not too different from that designed for high ash mixed waste residues could provide a high waste loading, high durability disposal medium. A close relative of zirconolite, the mineral pyrochlore, can be made with up to 50% by weight of UO_2. Our goal in waste form design then became the selection of a phase assemblage that could accommodate all three of the major waste types at Chernobyl using the same system of process chemistry. We would allow, however, differences in proportions of phases for each of the waste types and possibly differences in redox control to give maximum flexibility.

The first material that will have to be treated is the fuel dust and hot particles presently inside the sarcophagus. This material consists of fine grain sizes and will be the easiest to process into a high quality ceramic waste form because crushing to reduce the size of the particles will probably not be needed. The fuel dust will be predominantly UO_2 with about 1% of fission products and actinides. The fuel in Chernobyl Unit 4 at the time of the accident had burn-up between 7.5 and 13.5 MWd/kg, with an estimated average of 11.5 MWd/kg.[3] The inside of the sarcophagus is exposed to water through rain penetrating through cracks in the roof. In addition, water is sprayed inside the area to suppress the dust. Gadolinium has been added at various times to help ensure criticality control.[2] If the gadolinium is collected together with the fuel particles, it can be directly incorporated into the zirconolite phase in the waste form.

The phase assemblage recommended for the fuel dust is 60% zirconolite, 15% perovskite, 15% nepheline, 0 to 10% rutile, and 0 to 10% spinel. The redox state during processing should be controlled to ensure that Mo is sufficiently reduced so the soluble Cs_2MoO_4 does not form. Achieving this condition may require addition of some Ti metal to the mixture after calcination and prior to forming the final ceramic. Either hot pressing in bellows or HIP, or sintering of moderate sized cold-pressed disks under controlled atmosphere conditions could be used to make the final form. Studies of preparation of simulated waste forms using 10% U and 10% Gd are in process to evaluate the quality of the product as a function of preparation method.

The second material to be retrieved would most likely be the fuel fragments, or part of them. This material is present in rather large pieces that will need to be ground up to produce fine particles that could be mixed with ceramic precursor materials. We suggest that the materials be crushed under cryogenic conditions, probably liquid nitrogen. This would embrittle the cladding and fuel pellets and make crushing easier. It would also provide a liquid medium to control dust during the crushing. After crushing, the ceramic precursor materials could be mixed in while still under liquid nitrogen. Then the mixture could stand at room temperature, without application of additional heat, until the excess liquid nitrogen had evaporated. Once the fuel fragments are size-reduced, they should be processed using the same phase assemblage proportions as the fuel dust.

The final waste form for Chernobyl would immobilize the lavas. These materials are quite rich in silica, which is the reason we selected nepheline as the Cs host in the phase assemblage for all Chernobyl waste forms. It is possible that the lavas are very low in Cs themselves, but this would not cause us to alter our recommendation that nepheline be used as the Cs host phase. The lavas will need to be crushed to produce particles small enough to mix efficiently with the ceramic additives. The lavas should crush fairly readily, so an evaluation of the cost and need for use of liquid nitrogen versus crushing under water, but needing to dry the material after mixing in the precursors using a heat source should be done. The processing conditions for the lavas might require a different redox control, depending on the composition and redox state of the wastes. The other major difference between the lava waste forms and those for the other fuel materials is that nepheline would be in higher abundance and the zirconolite proportions would be reduced since there is less U to immobilize per unit mass. Variation of the phase proportions over large ranges does not change the processing temperature for this phase assemblage.[7]

V. CONCLUSIONS

We have evaluated the condition of the fuel-containing masses at the Chernobyl Unit 4 reactor site and developed a phase assemblage of titanate and silicate minerals to immobilize those materials for subsequent storage or disposal. The phase assemblage is identical to that developed to immobilize the residues from high ash content mixed wastes. The assemblage consists of zirconolite, nepheline, perovskite, and spinel. For fuel dust and fragments, the proportion of zirconolite would be high (60%); for the lavas, the proportion of nepheline would be high.

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