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FOREIGN TRIP REPORT

ORNL/FTR-2708

DATE: October 7, 1987

SUBJECT: Report of Foreign Travel by T. L. Sams, Project Engineer, Grout Technology Development Group, Chemical Technology Division

TO: Herman Postma

FROM: T. L. Sams

PURPOSE: To participate in a collaborative study of waste immobilization technology with scientists at the Centre d'Études Nucléaires de Saclay in France.

SITES VISITED:	8/29-9/28/87	Centre d'Études Nucléaires de Saclay (CEN-S)	Saclay, France	A. Bernard
	9/29/87	Centre d'Études Nucléaires de Fontenay-aux-Roses	Fontenay-aux-Roses, France	M. Jorda
	9/30-10/2/87	Centre d'Études Nucléaires de Saclay (CEN-S)	Saclay, France	A. Bernard

ABSTRACT: The traveler participated in a collaborative study of waste immobilization technology with scientists at the Centre d'Études Nucléaires de Saclay (CEN-S) in France. This assignment was implemented pursuant to the July 26, 1983, agreement between the Commissariat à l'Énergie Atomique and the U.S. Department of Energy in the field of Radioactive Waste Management. Efforts were focused on utilization of cements and technology currently used by CEN-S scientists to immobilize two low-level radioactive waste streams identified by scientists at Oak Ridge National Laboratory (ORNL). One waste stream contains typical decontamination waste (phosphate waste), and the other represents typical wastes currently found in the Melton Valley storage tanks at ORNL (nitrate waste). Formulation criteria for fluidity, structural durability, and retention of radionuclides were imposed on the immobilization study. Three types of French cement were evaluated for the nitrate waste, and four types of French cement were evaluated for the phosphate waste. Samples were

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prepared for durability and leachability testing for each of the waste streams.

At the Centre d'Études Nucléaires de Fontenay-aux-Roses, the traveler discussed 1) modeling long-term behavior of cement-based waste forms, 2) chemistry of the waste form, and 3) studies on radionuclide transport from waste forms.

Report of Foreign Travel to Saclay, France

August 28-October 2, 1987

Terry L. Sams

The purpose of the trip was to study the formulation of cement-based waste forms and to prepare waste-form samples. For the past six years, Oak Ridge National Laboratory (ORNL) has supported efforts by Rockwell Hanford Operations [now Westinghouse Hanford Company (WHC)] to build a Transportable Grout Facility (TGF) for the disposal of low-level liquid waste. ORNL has also supported internal efforts as well as those at Weldon Springs, Idaho National Engineering Laboratory, Y-12 Plant, and Oak Ridge Gaseous Diffusion Plant for the disposal of both low-level liquid wastes and sludges. These efforts have been oriented toward process engineering and the implementation of cement-based waste forms. However, the French are more interested in the materials science and basic mechanism aspects of cement-based waste forms. The efforts of the traveler and of French scientists are complementary and provide valuable technical information that is of interest to ongoing ORNL projects as well as to other U.S. Department of Energy (DOE) waste management programs. Areas of particular interest are 1) use of new materials and their effect on performance, 2) characterization of materials currently being used, and 3) full-scale leaching experiments. This assignment was implemented pursuant to the July 26, 1983, agreement between the Commissariat à l'Énergie Atomique (CEA) and the U.S. DOE in the field of Radioactive Waste Management.

August 31-September 28, 1987 - Centre d'Études Nucléaires de Saclay (CEN-S)

The traveler was assigned to CEN-S to participate in a cooperative effort to evaluate cement-based waste forms. A nitrate-rich low-level-waste stream, typical of the supernatant found in storage tanks, and a phosphate-rich low-level-waste stream, typical of decontamination waste, had previously been chosen for this study. The traveler spent the first week becoming acquainted with the various methodologies utilized by scientists at CEN-S. It was evident that their approach was through materials science and basic mechanism study, whereas the traveler approached the problem through process engineering and the implementation of cement-based materials. Discussions with A. Bernard, E. Revertegat, P. Bouniol, and R. Atabek established a protocol for preparation and evaluation of the waste forms.

The traveler and P. Bouniol held many discussions concerning the preparation and testing of the cement-based waste forms (grouts). The French scientists perform mixing of the dry materials, such as cement and sand, and of the grout in a manner much different from that to which the traveler is accustomed. To compare the grouts prepared in France to those prepared at ORNL, it was necessary for the traveler to set up and operate a viscometer, Rheomat 108 by Contraves. Measurements of shear stress as a function of shear rate could then be performed on freshly mixed grouts.

Other tests that were decided upon include 1) 28-d unconfined compressive strength, 2) 28-d flexive strength, 3) shrinkage and weight loss during a 28-d curing time, 4) X-ray diffraction analysis of the sample after 28 d, and 5) leaching of the grouts after 28 d.

The traveler met with E. Revertegat, A. Bernard, P. Bouniol, and R. Atabek to discuss preparation and compositions of the waste streams. It was evident that P. Bouniol was the principal engineer for grout formulation and that E. Revertegat was the principal scientist for materials testing, especially X-ray diffraction. A timetable was established for sample preparation and testing.

The traveler spent the majority of his time developing appropriate grout formulas for the two waste streams being studied. A specialty cement was acquired for use with the phosphate waste; this cement was comparable in composition to American Portland cements. Four types of cement were then evaluated for use with the phosphate waste. Only three types of cement were evaluated using the nitrate waste. Both waste streams were tested at two solids-to-waste ratios. Thus, the effects of different cements as well as waste stream chemistry could be studied. Samples were then prepared for all the previously mentioned tests for both waste streams during the next several weeks.

The French scientists explained that the precipitation of phosphate (PO_4^{3-}) by $Ca(OH)_2$ prior to mixing with dry materials would produce better grouts. Since phosphate is a set retarder, precipitation of the phosphate allows the grouting material to harden more rapidly. This fact was proven when samples were prepared using the phosphate waste and then tested for setting time (hardening of the material). This test is conducted on an automated Vicat apparatus at 15-min intervals until the grout hardens. This piece of equipment could be very cost effective in grouting studies performed in the U.S. Another piece of equipment that was used in France was a Shrinkage/Expansion tester; this equipment could be very useful in those projects where expansion or shrinkage of the grout is of concern.

Since the majority of tests are performed after a 28-d cure period, the traveler had to make rapid decisions as to what grout formulas would be investigated further. These decisions were based principally on the fluidity of the grout and its time of setting. Discussions were held with P. Bouniol and E. Revertegat after each experimental series to determine the best grout formulas. Formulation of grouts for the nitrate waste stream was more facile than for the phosphate waste stream, but formulas were chosen for both wastes, and an experimental plan was established. The plan includes a leach protocol using nonradioactive tracer elements as well as performance testing. These results will be available at a later date.

It was evident that the French are very interested in waste-form chemistry, as well as processibility and formulation techniques. Their principal criteria for waste-form development are 1) to maximize waste loading, 2) to minimize the release of radionuclides, and 3) to create a waste form processible with standard equipment. However, statistical

formulation techniques such as those used by the traveler are not normally utilized. Variations in the dry materials and the waste stream are not fully explored and thus could be an area of concern. The traveler provided R. Atabek and A. Bernard with copies of several publications which explain his formulation and data analysis techniques. They appeared very interested in our methodology as well as in our Quality Control/ Quality Assurance program. Several discussions were held on both of these subjects. R. Atabek expressed interest in another joint effort in the future so that our techniques could be more fully utilized and implemented.

The traveler met often with E. Revertegat to discuss analysis of the waste form. Her principal analysis technique is X-ray diffraction; she is interested in identification of the various phases within the waste-form matrix and correlating this information with performance. Two major areas of interest are shrinkage and leachability. Both of these areas have performance criteria and thus are taken into consideration when formulation of grouts is undertaken. The French scientists have a vast amount of experience and data concerning phase identification in the waste form. Correlations between waste-form phases and performance would be extremely beneficial in grout formulation. This information could also be useful in predicting long-term performance. The traveler feels that a detailed experimental effort using applicable statistical techniques should be undertaken; and the French were very receptive to this idea. Phase identification in the waste form is very important, so efforts should be made to follow this work more closely.

The traveler met with P. Conche to discuss his work on plasticizers, which are currently used in many grout applications in both the U.S. and France. Mr. Conche was interested in the effects of the plasticizers on waste-form durability. His investigations are currently on the use of Pozzolith 400 series plasticizers and their effect on air entrainment. His work clearly illustrates that some problems could arise if the proper additive is not chosen. For example, one of the plasticizers used in the investigation increased the amount of air entrainment but also caused phase segregation within the waste form. This resulted in a more dense material at the bottom and a very porous phase at the top of the sample. Also, the volume increased approximately 10%. This work would be of interest to anyone involved in waste-form development where the use of plasticizers is anticipated.

Discussions were held with M. Pigeon, a visiting professor from Université Laval in Quebec, concerning the use of plasticizers and air-entraining admixtures and their effect on grout durability. His work is particularly of interest to those concerned with freeze/thaw durability. Large-scale experiments have been performed in Canada to determine admixture effects on the durability of concrete in actual weathering conditions. Waste management programs where the waste form will be subjected to freeze/thaw cycles should follow his work in France and investigate his previous results.

One waste stream of mutual interest to the U.S. and France is cladding removal waste. The French have spent a lot of time and effort on

immobilization of the Zircaloy hulls. The traveler has spent over 18 months on grout formulation development for this waste stream in support of the TGF at Hanford. P. Bouniol is the principal investigator for the French study; thus, much time was spent in discussing our mutual work. The French immobilize the actual hulls, whereas our work involves immobilizing the waste stream after dissolution of the Zircaloy hulls. The traveler was shown full-scale samples of the immobilized waste form as well as full-scale equipment. Discussions on waste-form performance were held, and data were compared from our different approaches. The French have more stringent durability criteria than the ones imposed on our work; and the traveler's work on these waste streams was constrained by the stringent processibility requirements. Grouts produced in the U.S. are typically more fluid than the ones produced in France. This is particularly true for all work in support of the TGF and in situ grouting. However, the work by the French in this area is of great interest and should be investigated further.

The traveler met with J. C. Nominé on several occasions to discuss leaching experiments, which Mr. Nominé is currently conducting, on full-scale blocks of actual immobilized waste. Recent publications on his work illustrate that some scale effect may exist on the leachability of material. His experiments involve samples of 0.2, 2, 20, and 200-L size that were prepared at the same time and from the same batch to maximize homogeneity. Normally, extrapolation of data from small samples is expected to be representative of the leachability of full-size samples. But even when the data were corrected by the volume-to-surface ratio, as in the American Nuclear Society leach protocol 16.1, this was not necessarily the case. His results are very interesting, and currently he cannot offer a complete explanation for this scale effect on the leachability of his samples. The traveler was asked to review a future publication and to provide an opinion as to the interpretation of the results. The data presented in this future publication are for a much longer time frame than previously published. Mr. Nominé was very open with his results and provided the traveler with new data to bring back to ORNL for evaluation. This work is very important and should be followed by scientists involved in waste management activities in DOE.

<u>September 29, 1987 - Centre d'Études Nucléaires de Fontenay-aux-Roses (CEN-FaR)</u>

The traveler and A. Mattus, an ORNL scientist, were invited to CEN-FaR by M. Jorda and R. Atabek. The trip was of an informative nature and many laboratory visits were conducted. Discussions were held with 1) A. Lajudie, study of clays and their effects on waste-form properties; 2) J.-C. Petit, long-term leaching behavior of cement-based waste forms; 3) J. P. Mangin, modeling of leach behavior; 4) A. Vitorge, chemistry of radionuclides; 5) J. Oliver, transfer studies of radionuclides, and 6) G. Baudin, Chief, Department de Recherche et Développement Déchets. Of particular interest was the work being performed by J. Oliver on the transfer of radionuclides into the environment through the waste form. J.-C. Petit is involved in studies on the long-term behavior of cement-based grouts, including work on an 1800-year-old Roman pozzolanic

grout. His study confirms results from Penn State work suggesting that high-silica pozzolanic formulas are good choices for waste forms. A. Lajudie discussed water diffusion coefficients for clay-containing additives in cement, which are the same as those measured at ORNL (approximately 10^{-8} cm^2/s). The traveler expressed interest in the work of these three scientists and feels that DOE could benefit from their respective studies.

<u>September 30-October 2, 1987 - Centre d'Études Nucléaires de Saclay (CEN-S)</u>

The traveler met with R. Atabek, A. Bernard, P. Bouniol, and E. Revertegat to discuss the results obtained during his visit. Mr. A. Mattus of ORNL was also present at these meetings. The traveler explained his methodology and criteria used for choosing grout formulations. The traveler and R. Atabek decided that samples would be prepared at CEN-FaR using radioactive materials for leach testing and that A. Mattus would write up a leach protocol and follow the progress of the experiments. The traveler informed all personnel at these meetings of the proposed timetable for completion of all testing on the grout samples. A. Mattus will be responsible for obtaining the test results and correlating the work activities. R. Atabek wants to maintain contact with ORNL personnel and hopes that future cooperative studies can be arranged.

SUMMARY AND CONCLUSIONS

The French approach to waste-form development is oriented toward materials science, and they are very interested in basic mechanism studies. Emphasis is placed on determining why retention of radionuclides occurs and what phases in the waste form are most responsible. They utilize X-ray diffraction for solid analysis and have developed an expertise in this field. The process engineering aspect of waste-form development is considered secondary and more easily manipulated. They have an ongoing leach study of full-scale waste forms and are studying the basic mechanisms of leaching. The effect of plasticizers and clay additives on waste-form chemistry is another area of importance to the French.

The U.S. could learn much from the French in the area of waste-form chemistry and solid analysis; their full-scale leaching tests should be closely followed and evaluated. In turn, the French could benefit from our expertise in statistical formulation development and process engineering. This joint effort provided much insight into basic mechanisms of retention, and the technology obtained will prove to be very useful.

APPENDIX A

Itinerary

August 28-29, 1987	Travel to Saclay, France
August 30-September 28, 1987	Saclay, France
September 29, 1987	Fontenay-aux-Roses, France
September 30-October 2, 1987	Saclay, France
October 3, 1987	Return to Knoxville

APPENDIX B

Persons Contacted

André Bernard	CEA, Saclay, France
Elaine Revertegat	CEA, Saclay, France
Pascal Bouniol	CEA, Saclay, France
Pascal Conche	CEA, Saclay, France
Jean-Claude Nominé	CEA, Saclay, France
Guy Baudin	CEA, Fontenay, France
Michel Jorda	CEA, Fontenay, France
Rosemarie Atabek	CEA, Fontenay, France
A. Lajudie	CEA, Fontenay, France
Jean-Claude Petit	CEA, Fontenay, France
J. P. Mangin	CEA, Fontenay, France
A. Vitorge	CEA, Fontenay, France
J. Oliver	CEA, Fontenay, France
Michel Pigeon	Université Laval, Sainte-Foy, Quebec
Theodore W. Bremner	University of New Brunswick, Fredericton, New Brunswick

APPENDIX C

Literature Acquired

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4. P. E. Rushbrook, G. Baldwin, C. G. Dent, "A Quality Assurance Procedure for Use at Treatment Plants to Predict the Long-Term Suitability of Cement-Based Solidified Hazardous Wastes Deposited in Landfill Sites," Environmental Safety Centre, Harwell Laboratory, DIDCOT, OX11 ORA, United Kingdom.

5. P. Bouniol, Rapport Technique Études des Mecanismes de Piegeage du Cesium par des Melanges Additif-Ciment Pour le Conditionnement des Dechets Nitrates, Contract CCE N° WAS-441-85-13 F, D.R.D.D. n° 123, F.A 6760-13, Février 1987.

6. P. Bouniol, Note Technique Étude des Mecanismes de Piegeage Du Cesium par des Melanges Additif-Ciment Pour le Conditionnement des Déchets Nitres, Contrat CCE n° WAS-441-85-13 F, N.T. SESD/86.34, FDP n°, F.A. n° 6760.13, Juillet 1986.

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8. J. C. Nomine, A. Billon, "Experience Acquired in the Field of Long-Term Leaching Tests on Blocks of Radioactive Waste," Department de Recherche et Développement Déchets Service d'Étude des Stockages de Déchets, 4th International Hazardous Waste Symposium on the Environmental Aspects of Stabilization/Solidification of Hazardous and Radioactive Wastes, Atlanta, Georgia, 3-6 May 1987.

9. P. Robouch, P. Vitorge, $PuO_2(CO_3)$ Solubility, C.E.A., Centre d'Études Nucléaires – IRDI/DERDCA/DRDD/SESD/SCPCS/LCh.

10. P. Robouch, P. Vitorge, "Solubility of $PuO_2(CO_3)$," Inorg. Chim. Acta, 140, Elsevier Sequoia, Switzerland (0020-1693/87).

11. Ch. Riglet, P. Robouch, P. Vitorge, "Standard Potentials of the (MO_2^{2+}/MO_2^{+}) and (M^{4+}/M^{3+}) redox systems for neptunium and plutonium," IRDI/DERDCA/DRDD/SESD/SCPCS, Commissariat à l'Énergie Atomique.

12. V. Moulin, P. Robouch, P. Vitorge, B. Allard, Environmental Behaviour of Americium in Natural Waters, DERDCA/DRDD/SESD/SCPS, Centre d'Études Nucléaires de Fontenay-Roses.