U-006-306.18

3475

RESPONSES TO THE OPERABLE UNIT (OU) 4 VITRIFICATION STUDY CONDITIONAL APPROVAL

5-27-92

DOE/OEPA
DOE-1773092
6
LETTER

[redacted]

3475

Department of Energy
Fernald Environmental Management Project
P.O. Box 398705
Cincinnati, Ohio 45239-8705
(513) 738-6357

MAY 27 1992

DOE-1773-92

Mr. Graham E. Mitchell, Project Manager
Ohio Environmental Protection Agency
40 South Main Street
Dayton, Ohio 45402-2086

Dear Mr. Mitchell:

RESPONSES TO THE OPERABLE UNIT (OU) 4 VITRIFICATION STUDY CONDITIONAL APPROVAL

The following responses are provided to address your enclosed comments received on the subject document.

The Health and Safety Plan for the vitrification work being done by Battelle Pacific Northwest Laboratory (PNL) is located in Appendix B of the report.

In addition to the Product Consistency Test (PCT) that will be done during treatability, the Feasibility Study (FS) for OU 4 will further evaluate vitrification of the waste according to the criteria as required to complete the FS.

The response to the article on the potential effects of humic acid on vitrified waste is enclosed.

If you or your staff have any questions, please contact Randi Allen at FTS/Commercial 513-738-6158.

Sincerely,

Jack R. Craig
Fernald Remedial Action
Project Manager

FN:Allen

Enclosure: As Stated

Recycled and Recyclable

cc w/enc.:

J. J. Fiore, EM-42, TREV
K. A. Hayes, EM-424, TREV
J. Benetti, USEPA-V, AT-18J
M. Butler, USEPA-V, 5CS-TUB-3
J. A. Saric, USEPA-V, HRE-8J
J. Kwasniewski, OEPA-Columbus
P. Harris, OEPA-Dayton
M. Proffitt, OEPA-Dayton
T. Schneider, OEPA-Dayton
T. W. Hahne, PRC
L. August, GeoTrans
R. L. Glenn, Parson
D. J. Carr, WEMCO
L. S. Farmer, WEMCO
J. P. Hopper, WEMCO
J. D. Wood, ASI/IT
J. E. Razor, ASI/IT
AR Coordinator, WEMCO

OhioEPA
State of Ohio Environmental Protection Agency

Southwest District Office
40 South Main Street
Dayton, Ohio 45402-2086
(513) 285-6357
FAX (513) 285-6404

LOG F-3145
FILE
LIST

MAY 15 10 47 AM '92

U-0067 707.41 3475
3264

George V. Voinovich
Governor

May 14, 1992

Re: O.U. 4 VITRIFICATION STUDY
CONDITIONAL APPROVAL

Mr. Jack R. Craig
Project Manager
U.S. DOE FEMP
P.O. Box 398705
Cincinnati, Ohio 45239

Dear Mr. Craig:

The purpose of this letter is to conditionally approve the O.U. 4 Vitrification Study. This approval does not include the Health and Safety Plan per Ohio EPA policy. The conditions for approval are that DOE address the two issues listed below in the O.U. 4 Feasibility Study.

General Comments

1. Ohio EPA still has a concern about the physical/structural integrity and durability of the vitrified product. Our concern is that a product that maintains its shape and integrity is essential to any scenario which incorporates storage and subsequent retrieval of the waste for disposal. Ohio EPA expects that this concern will be addressed by DOE within the Operable Unit 4 Feasibility Study.

2. During the March 31 project managers meeting, Ohio EPA provided DOE with an article describing the potential effects of humic acid on vitrified waste. Ohio EPA expects that DOE will investigate this information and either incorporate it into an optional phase of testing or somehow address it within the Operable Unit 4 Feasibility Study.

If you have any questions about these conditions, please contact Tom Schneider or me.

Sincerely,

Graham E. Mitchell
Project Manager

GEM/acn

cc: Jenifer Kwasniewski, DERR
Tom Schneider, DERR
Jim Saric, U.S. EPA
Dennis Carr, WEMCO
Lisa August, GeoTrans
Tom Hahne, PRC
Robert Owen, ODH

(Allan)
Partial Action Response
to T-1360
(4265)

Printed on recycled paper

14 Vitrification

3475

Behavior

Provided by Tom Schroeder - OEPA 3/31/92

Traumatic Holocaust legacy

A large proportion of Jewish survivors of the Nazi Holocaust – particularly those who endured extreme atrocities in concentration camps – suffer from post-traumatic stress disorder (PTSD) nearly 50 years after World War II, according to a report in the March AMERICAN JOURNAL OF PSYCHIATRY.

Studies of prisoners of war have documented high rates of PTSD up to 35 years after release from captivity (SN: 2/2/91, p.68), but few follow-up studies of Holocaust survivors have emerged in the last two decades.

Of 123 Jewish survivors living in the Toronto area and applying for compensation from the German government, 58 suffer from PTSD, assert psychiatrist Klaus Kuch and psychologist Brian J. Cox, both of the University of Toronto. PTSD symptoms include recurring memories and nightmares of traumatic experiences, emotional detachment from loved ones, extreme suspicion of others, difficulty sleeping and avoidance of any situation reminiscent of past traumas.

The sample included 78 people who had been confined in concentration camps for an average of nearly 15 months (including 20 who faced extreme atrocities and the constant threat of death at Auschwitz), and 45 individuals who had been in labor camps and ghettos or had hidden with families that offered shelter to Jews. Half of the concentration camp survivors – and 13 of the Auschwitz survivors – suffer from PTSD, compared with about one in five survivors who had not been incarcerated in concentration camps.

Only a small minority of Holocaust survivors reported receiving psychotherapy or other psychiatric care at any time following the war, the researchers note. Survivors may avoid mental health treatment because they are demoralized or fear reexperiencing past traumas, and physicians may avoid taking detailed histories of brutality and thus miss many PTSD cases, Kuch and Cox contend.

A suicidal combination

People with a history of both severe depression and headaches accompanied by sensations known as auras experience a greatly increased likelihood of thinking about and attempting suicide, asserts psychologist Naomi Breslau of Henry Ford Hospital in Detroit. Migraines heralded by aura symptoms, such as ringing in the ears, nausea, blurred vision or extreme sensitivity to light, boost the already elevated risk of suicide among severely depressed individuals, Breslau contends in the February NEUROLOGY.

The brain chemistry linking migraines with auras and severe depression to suicide attempts remains unclear, she says. However, other research has found abnormalities in the chemical messenger serotonin for all three conditions.

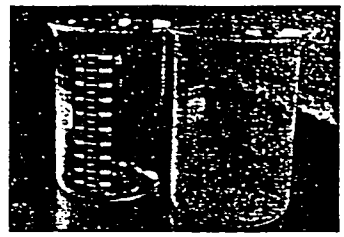
Breslau and her colleagues interviewed a random sample of 1,007 adults, ages 21 to 30, who belong to a Detroit-area health maintenance organization. Of 788 "control" participants reporting neither migraines nor severe depression, about 2 percent noted past suicide attempts. About the same rate of suicide attempts appeared among 51 volunteers who experienced no depression and who had migraines without auras.

In contrast, 14 of 26 adults who suffered severe depression as well as migraines with auras had attempted suicide – by far the highest rate of any group in the study. Suicide-attempt rates of 33 participants reporting only migraines with auras, 91 reporting only severe depression and 18 reporting migraines without auras plus severe depression also markedly exceeded the control rate, but to a considerably lesser degree.

Volunteers with a background of depression and migraines with auras also reported substantially more prior thoughts about death and suicide, and far more periods during which they wanted to die, than any other group.

Chemistry

Of humus, glass beakers and radwastes



Marley

Foreground beaker shows etching by dilute humics.

In tanks at several federal facilities, the Department of Energy (DOE) maintains huge stores of highly radioactive defense wastes. The 177 tanks at its Hanford Site in Richland, Wash., for example, hold between 55,000 and 1 million gallons each. Concern over leaks of radioactive wastes at Hanford – totaling some 750,000 gallons – has added urgency to DOE's waste-solidification program. Later this year, the agency plans to begin demonstrating vitrification (incorporation into glass) of sludges distilled from liquid radwastes, according to DOE spokesman Fred Lash. Full-scale waste vitrification may begin next year, he says, initially at DOE's facility in Savannah River, S.C.

DOE chose to stabilize its wastes in borosilicates, Lash explains, because of all solids, these glasses are "probably the most stable and insoluble." Borosilicates will not break apart, even if subjected to large amounts of water and heat, he says. But DOE aims to prevent such aqueous encounters by sealing vitrified wastes in stainless steel drums at very dry hideaways.

Experiments now under way at another DOE facility underscore the wisdom of taking those additional precautions: The tests indicate that natural organic hydrocarbons present in even pristine groundwater can leach radioactive materials from borosilicate glass, dissolving them in the water.

As leaves and other plant materials decay into humus, they create a mix of complex hydrocarbons known as humic acids. At Argonne (Ill.) National Laboratory, Jeffrey S. Gaffney has been studying humic acids' ability to leach radium, thorium and uranium from rocks and sand – and to transport the radionuclides long distances in water. Though ubiquitous at widely varying concentrations in soil, lakes, springs and even groundwater, humic acids "have been ignored in the models to determine whether [borosilicate] glasses will be stable" over the centuries they must bind radioactive wastes, points out Argonne chemist Nancy A. Marley. That oversight could prove important, Gaffney believes, since their work indicates that humic acids "are [chemically] active, even at fairly low concentrations." Indeed, he notes, "they literally etched the [borosilicate] glass of a new beaker in just a few hours."

Marley made that discovery a few years back when she inspected the apparent residue left by bog water boiled in the beaker. Close examination revealed that "natural humics in the water had actually removed silica from the beaker," clouding its surface, she recalls. The finding, which Marley is preparing for publication, initially surprised the two researchers: Beakers are supposed to be nonreactive, and the water in this one had a pH of only about 6, typical of normal rain.

Marley and Gaffney now suspect that carboxylate (COO-) sidegroups are a predominant constituent of the still largely uncharacterized humic acids. Carboxylates would explain the high solubility – and therefore the long lifetime in water – of the organic hydrocarbons, Gaffney asserts. That carboxylates "are fairly active binding agents for free metals" might also help explain their affinity for the radionuclides, he adds.

But could humics actually leach radionuclides from glass? Preliminary findings of tests begun at Argonne last month by Marley, Gaffney and Ken A. Orlandini indicate that the water-borne acids indeed removed uranium from borosilicate glass and held it in the water. This suggests that even if such a process were allowed to proceed very slowly in nature, "over the years it's going to be important," Marley says.

4

From: R. A. Vogel (6748) WEMCO:ER:OU4:92-041

Date: April 13, 1992

Subject: THE STABILITY OF BOROSILICATE GLASS IN THE PRESENCE OF HUMIC ACIDS

To : J. P. Hopper

The question has recently been raised about the stability of borosilicate glass when exposed to humic acids. This question arose as the result of an article in Science News which described the experiences of individuals at Argonne National Laboratory with humic acids and glass. These individuals made the observation that humic acids can react with the glass of a beaker and in separate test, that humics can remove uranium from borosilicate glass. Without questioning these observations, perhaps it is important to consider the role of humic acids in the environment.

The article correctly points out that humic acids "are (chemically) active, even at fairly low concentrations." This is not new information, this has been understood in ecological studies at least since the late 60's. The article then discussed the fact that humic acids are ubiguitous in natural systems, but then conveys the message (perhaps unintentionally) that these acids are a significant component of these systems in terms of volume. Although very significant in the functioning of natural systems, it is misleading to think of humic acids permeating the environment in concentrations which would react vigorously with glass. If this concept were extended to the environment, as a whole, the result would be the solubilizing of most material. I don't think this is a good perspective from which to view the significance of an interaction of humic acids and borosilicate. The solubilizing does occur, but at a rate that maintains natural systems.

It would not be surprising if in ongoing tests Argonne found that humics do leach various substances from borosilicate glass. The questions that must be asked are, at what rate and what combination of chemical entities comprise what Argonne is terming humic acid? This rate of leaching, considered against the occurrence of humic acids in onsite or offsite disposal will determine the significance of this issue. It is suggested that OU4 develop and maintain communication with the Argonne team, once substantive tests have been accomplished. With quantitative data from these tests a realistic understanding of the issue can be developed.

Battelle PNL was contacted to determine their position on humic acids, the response is attached.

If there are any questions, please contact me at the above extension.

Robert A. Vogel

R. A. Vogel
Operable Unit 4

RAV:lem

Attachment

c: R. B. Allen, DOE-FN
D. J. Carr
I. W. Diggs
Y. G. Gale
H. H. Glassey
L. A. Heckendorn
D. A. Nixon
S. A. Radabaugh
W. G. Tope

AR Files
ERA Project Files
Central Files

3475

Battelle - Pacific Northwest Laboratory

Chris Chapman
Mail Stop P7 - 41
P.O. Box 999
Richland, WA 99352
Phone: (509)-376-6576 FTS: 444-6576
FAX: (509)-376-1867 FTS: 444-1867

APPLIED MELTER TECHNOLOGIES GROUP
WASTE TECHNOLOGY DEPARTMENT
WASTE TECHNOLOGY & ENGINEERING CENTER

"Putting Technology to Work"

WASTE → GLASS

today's date: 11 April, 1992

Send to FAX # **FTS 774-8943**
Deliver to ⇒ Bob Vogel, Westinghouse Fernald

Bob,
Dan asked me to respond to a question of humic acid on glass. Apparently, someone is extrapolating the article or note in SCIENCE NEWS by someone from Argonne to have significance with a decision with OU#1 or OU#4. I do not had any direct experience with this acid and waste glass but have the following general comments.

Some of our chemists have experience with humic acid which is described as a very weak acid but seriously doubt it has any significant reaction with glass or at least they haven't observed "etching" of Pyrex by it. The note in SCIENCE NEWS appears to be contrary to their experience.

Humic acids have and are continuing to be evaluated as being a potential means for increasing the transport rate of radioactive consistuents such as TRU elements away from a hypothetical deep repository. It apparently can complex quite well with selected elements and augment its transport through ground water more rapidly than without humic acid. Many things are considered when trying to estimate potential releases at 100,000 to 1,000,000 years into the future. However, it has not been considered as a significant leachate for the glass waste form.

If humic acid were a significant leaching compound of silicates, soils would have lost a significant amount of silica. This is not my understanding of soil compositions. Thus, millions of years of humic acid leaching of silicates has not been significant in nature. For me this seems to refute the concern about humic acid. I believe water alone has a greater influence on destruction or dissolution of silicates. Man made artifacts have similarly endured tens, hundreds, even thousands of years in moist soils with humic acid. The dominant loss mechanism is again water leaching. Leachates with glass typically result in a higher pH which would neuralize acids. For this condition, humic acid may reduce glass leaching.

For humic acid to have a significant impact on glass dissolution and radioactive release, large quantities of acid (water) would need to be transported to the bulk glass and away from it for a very long time. This also seems unlikely for any reasonable disposal scenario.

Although I have no currently available experimental evidence, it appears to me that someone may have amplified a simple, unusual laboratory experience too far.