



UNITED STATES DEPARTMENT OF COMMERCE  
National Bureau of Standards  
Gaithersburg, Maryland 20899

March 15, 1988

Dr. Michael Tokar, Section Leader  
Low-Level Waste Management and  
Decommissioning NMSS  
U.S. Nuclear Regulatory Commission  
11555 Rockville Pike  
Rockville, MD 20852

Dear Dr. Tokar:

I have prepared the attached comments addressing some issues and questions raised at the February 1988 meeting with LN Technologies. Hopefully, they will be of assistance to you.

Sincerely,

A handwritten signature in cursive script, reading "James R. Clifton".

James R. Clifton

enclosure

8803220090 880315  
PDR WASTE  
WM-20 DCD

WM-20  
NLDI 1/1

COMMENTS ON FEBRUARY 24-25, 1988, MEETING BETWEEN NRC AND LN TECHNOLOGIES

The following issues and questions were among those raised in the discussions held during the February 24-24, 1988, meeting between NRC and LN Technologies. Further consideration of their implications was regarded as being needed.

1. Effect of temperature of boric acid waste form
2. Sulfate concentration and cement durability
3. Leaching of calcium
4. Relationship between small laboratory and large field specimens
5. Effects of insoluble residue from filtration

Comments regarding these issues and questions are presented in the following.

1. Effect of Temperature of Boric Acid Waste Form The staff of LN Technologies (denoted as LN) disclosed that the temperature of aqueous solutions of boric acid waste sometimes approached 100°C (212°F), prior to be mixed with portland cement. What effect will elevated temperatures have on the stability of the cement solidified LLW materials.

COMMENT - The effects of such a high temperature on the properties of the cement solidified LLW depends on the temperature of the mixture when the cement and any addition mix water are combined with the solution of boric acid. If the temperature of the mixture is less than 45°C (115°F), neither the chemical or the physical properties of the hydrated cement should be significantly changed. Some reduction in strength may be found as the temperature increases from around 20°C (68°F) to 45°C (115°F) because that hydration products will not be uniformly distributed. The chemistry and form of the hydration products will change as the temperature is increased from around 45°C (115°F) towards the boiling point of water. The calcium-silicate-hydrate (C-S-H) formed from the hydration of tricalcium silicate and dicalcium silicate will become more crystalline, forming a phase which has an increased density and smaller volume than C-S-H, leaving voids in the cement matrix. Thus the porosity of the hydrated cement paste and its strength will be substantially reduced. To avoid this problem when autoclaving cement products, reactive silica is added which favors the formation of a poorly crystalline C-S-H and eventually to tobermorite gel. The hydrated cement matrix with the tobermorite gel has improved strengths.

Because temperature variations undoubtedly will have a significant effect on the properties of the cement solidified LLW, the laboratory conditions should simulate those experienced during the field preparation.

2. Sulfate Concentration and Cement Durability One waste form that LN is solidifying with cement contains an appreciable amount of soluble sulfates. If hardened concrete is exposed to aqueous solutions of sulfate ions, an expansive reaction may occur which causes the cracking and disintegration of concrete. Will a similar process occur with the solidified LLW?

COMMENT - Sulfates can attack cement through at least two reactions: reaction between the tricalcium aluminate ( $C_3A$ ) in portland cement to form ettringite; and a reaction with calcium hydroxide to form calcium sulfate. Ettringite ( $C_3A \cdot 3CaSO_4 \cdot 31H_2O$ ) occupies substantially more volume than its solid constituents and thus is an expansive product. If ettringite is formed before the cement matrix is firmly established, the matrix can compensate for the ettringite and cracking will not occur. When sulfate is mixed with the cement during mixing with water, ettringite will rapidly form - before the matrix has hardened. The second reaction, formation of calcium sulfate, results in a salt which is more soluble than calcium hydroxide and, therefore, more likely to be leached by groundwater. Thus, the most important process with regards to stability of cement solidified LLW appears to be the formation of calcium sulfate. Its rate of leaching will depend on the velocity of groundwater movement at the disposal sites. It should be noted that the above seemingly simple system can become quite complex over 300-years. For example, if all of the calcium hydroxide is converted to calcium sulfate then the pH of the pore solution and the chemistry of the hydrated cement paste will be drastically change. However, if insufficient sulfate is present to react with all the calcium hydroxide then ettringite decomposition and reformation could take place.

3. Leaching of Calcium Studies by LN (LN's Topical Report) indicate that 0.3% w/o of the calcium of the cement was leached in 90-days from a sodium sulfate waste specimen. Based on this leaching rate the calcium would be completely removed from the cement in less than 100-years. Yet, LN states that the solidified waste will maintain its integrity for 300-years.

COMMENT - During the leaching of portland cement, the alkali hydroxides would first be removed and the pH of the pore solution in the cement would be above 13. After the alkalies are leached, the pH will drop to 12.6 and calcium hydroxide leaching would occur. Then, after calcium hydroxide is leached, the C-S-H would begin to dissolve and the pH would decrease to around 11. C-S-H has a very low solubility and its leaching would be at a much lower rate than the hydroxides. Thus a leach rate of 0.3% per 90-days can not be simply extrapolated to predict service life. The apparent high leach rate observed by LN may be associated with the dissolution of calcium sulfate formed from the reaction of sulfates with calcium hydroxide. Also, the calcium ions will probably be leached more rapidly in distilled water than most groundwaters. The seriousness of the observed high leaching rate could be better evaluated after allowing the cement-sodium

sulfate waste specimens to remain in contact with the water for at least another 90-days (preferably longer, e.g., one-year) and periodically take measurements of the amount of calcium in the water.

#### 4. Relationship between Small Laboratory and Large Field Specimens

The approach used by LN for predicting the strength of large field prepared specimens is based on maintaining the same curing temperature for small laboratory specimens.

COMMENT - The approach used by LN is well-conceived. It is recommended that the internal temperatures of large field prepared specimens be measured and used in the laboratory accelerated curing. Also, the strength of laboratory specimens should be compared with the strength of cored specimens to determine the extent of correlation.

5. Effect of Insoluble Residue from Filtration An analysis of an insoluble residue found in the filtration of a waste form was made. Questions regarding the effects of the residue constituents on the performance of cement were raised.

COMMENT - It is assumed that the elements identified are in insoluble forms of metals, and oxide, hydroxide, and carbonate salts. If they are cations of soluble salts then the following comments may not be valid, depending on the specific anion. The following elements will not cause any difficulties: Zn, Cu, Ni, Cr, Fe, Si, and Na. Sodium, Na, could cause difficulties if an alkali-aggregate reactive aggregate was present. Boron, B, presumably in the form of a borate, can retard the setting of cement. Only if retardation is observed when solidifying the waste form with cement would the presence of boron cause any concern. Magnesium and calcium oxides can cause problems with the stability of hydrated cement pastes if they have been heated to an elevated temperature (above 800 to 900°C). Magnesium and calcium oxides heated to such temperature are called "dead-burned" because they react very slowly with water. It is doubtful that dead burned oxides are present. Magnesia, manganese oxide, can somewhat reduce the strength of hydrated cement if present in amounts greater than 5%, based on the weight of cement. Aluminum oxide is probably fused, which is a harmless form. The main concern with aluminum arises when it is in the form of tricalcium aluminate. It does not appear that any of the listed elements will cause any significant problems, in the reported proportions, presuming that they are in the form of metals, oxides, hydroxides or carbonates.