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**Civilian Radioactive Waste Management System
Management and Operating Contractor**

CONCRETE CHEMICAL EVOLUTION

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1. OBJECTIVE AND SCOPE

1.1 INTRODUCTION

The objectives of this analysis are to discuss and evaluate testing results that were performed for the M&O by the Pennsylvania State University (PSU) to evaluate the potential long-term evolution of organic admixtures in cementitious materials at elevated temperatures. The testing was designed to help provide a basis for a determination by the Performance Assessment group (PA) of the long-term acceptability and longevity of cementitious materials for repository use. The main purpose of the testing was to assess the evolution of gases (especially CO₂) from hydrated cement paste at elevated temperatures and to determine the impact on alkalinity, i.e., the pH value of cement paste pore solution. This information in turn can be used as scoping information to determine if further tests of this nature are needed to support PA.

As part of this discussion and evaluation of the PSU results, an assessment of alkalinity in a "cementitious repository" and an evaluation of organic materials are presented.

1.2 QUALITY ASSURANCE

This design analysis activity has been evaluated in accordance with QAP-2-0 and has been determined to be not quality affecting, based on the scoping nature of this study. It has been prepared based on NAP-MG-012, *Development of MGDS Technical Document Not Subject To QARD Requirements*.

The input data used in this task are preliminary and unqualified, therefore, the outputs are also unqualified. Because of the preliminary nature of this analysis, unqualified data are not identified and the formal TBV and TBD tracking system described in NLP-3-15, Rev 4, *To Be Verified (TBV) And To Be Determined (TBD) Monitoring System* is not applied. The output from this analysis will not be used for procurement, fabrication, or construction.

1.3 BACKGROUND

Currently, Repository Subsurface Design is considering concrete linings as the reference design for ground support in the emplacement drifts (Ref. 8.1). These linings will provide for the stability of the emplacement drifts throughout the preclosure period. However, cementitious materials in the repository drift environment during the postclosure period may have some adverse geochemical effects due to high pH pore solutions, typically from 12 to 13, in concrete fabricated with ordinary portland cement.

In order to mitigate the potential problems associated with high pH solutions, cement can be engineered by adding pozzolans such as silica fume (Ref. 8.10) to reduce the pH values. Based on the Performance Assessment (PA) Group's recommendation, a pH of about 10 or lower (Ref.

8.5) is desirable to increase the long-term geochemical stability of the repository system. However, the addition of silica fume to cement increases the plastic viscosity of the paste, and a large addition of silica fume to cement may cause a workability problem. Therefore, it is generally necessary for cement-silica fume systems, that a plasticizer or superplasticizer (both organic admixtures) be added for deflocculating the paste. However, the use of the organic admixtures in the repository environment may cause other postclosure performance problems related to waste package corrosion and waste isolation. For these reasons, it is important to determine the evolution of organic materials that will remain in the concrete as a function of time and repository thermal conditions. Consequently, a testing program was conceived by PA and implemented by Repository Subsurface Design to determine the effect of elevated temperature on organic admixtures in concrete.

1.4 METHOD

The methods used in this analysis include literature surveys, meetings with affected groups (especially PA), consultation with industry practitioners, and review of the results of the laboratory testing program conducted for this study.

2. REQUIREMENTS

The following requirements applicable to this analysis are specified in the document "Ground Control System Description Document" (Ref. 8.2) for ground control systems of repository openings.

2.1 OPERATIONAL LIFE

The ground control system shall fulfill the system functions during the operational life of 150 years. [Ref. 8.2: Section 1.2.2.1.6]

2.2 DURABILITY

The ground control system shall use durable, non-combustible and heat-resistant materials having acceptable long-term effects on the ability of the engineered barrier system to assure waste isolation, including postclosure conditions. [Ref. 8.2: Section 1.2.2.1.1]

3. ASSUMPTIONS

The following assumptions were made in order to perform the analysis.

- 3.1 Lining and grouting materials may be used in repository construction if it has been shown that their use does not adversely impact waste isolation nor interfere with required testing activities. They will be evaluated for chemical reactions that may adversely impact waste isolation. (Ref. 8.31, CDA: EBD RD 3.2.3.3.A.13)
- 3.2 A single ground support type will be used in emplacement drifts. Candidate ground support types under consideration:
 - Precast concrete
 - Cast-in-place concrete
 - Steel sets (Ref. 8.31, CDA: DCSS 034)
- 3.3 Maximum allowable preclosure rock surface temperature in emplacement drifts is 200 °C. (Ref. 8.31, CDA: DCSS 023)
- 3.4 Organic materials are restricted for use as rock support and other postclosure permanent material in all openings. Concrete (subject to restrictions on chemical composition of cementitious materials) and steel are allowable preclosure construction materials in all openings. (Ref. 8.31, CDA: DCSS 027)
- 3.5 The pore solution of the cement paste will have target pH values lower than 10 to minimize the potential geochemical impacts to waste isolation during the postclosure period in the repository environment (Ref. 8.5, cover page).
- 3.6 The water-cementitious material ratio for the concrete mixes will be assumed to be between 0.4 and 0.5 to ensure adequate strength and long-term durability.
- 3.7 Silica fume is to be used in the concrete to increase the strength and to reduce pH value of cement paste pore solution.
- 3.8 High-range water reducer (also called superplasticizer) will be used in the concrete to increase the workability.

4. LABORATORY TESTING

4.1 GENERAL

It is expected that the postclosure emplacement drifts will be very dry and at temperatures above 100°C for an extended period of time. In order to determine the effect of this dry and elevated temperature environment on the organic admixtures in the concrete, it was postulated that the organic admixtures would be decomposed and volatilized as gases, mostly CO₂ with other minor components such as SO₂ and NO_x.

The common backbones of most organic admixtures are carbon chains. During hydration of cement, the carbon chains of the organic admixtures may be disintegrated into forms with shorter carbon chains (lower molecular weights) and strongly adsorbed on the hydrated phases. Portions of the CO₂ gas evolved are likely to escape into the emplacement drift and repository rock. Remaining portions of the CO₂ gas evolved could react with the cement hydrated phases (such as portlandite Ca(OH)₂, calcium silicate hydrate (C-S-H) phases, and other hydrated phases). This reaction would result in the formation of calcium-carbonate minerals, mostly calcite (CaCO₃). This process is called carbonation and consumes the hydrated cement phases, especially portlandite, which is responsible for generating the pore solution at pH of 12 to 12.5. Thus, the carbonation process lowers the pore solution pH. More importantly, as a result of this evolution of the organic admixtures, the quantity of organic materials in the concrete may be reduced to a level, which may be acceptable to PA for long-term postclosure performance of the repository.

In order to confirm the above postulation concerning organic decomposition, it was decided to conduct some basic laboratory tests on cement-paste samples prepared with different types of candidate commercial superplasticizers. The Materials Research Laboratory (MRL) of the Pennsylvania State University (PSU) was selected to perform this testing program due to their leading expertise in this area. The test program has been successfully completed and details are presented in the final report "Laboratory Testing of Evolution of Organic Admixtures in Concrete", which is attached to this analysis. In the following sections, the objective, test matrix, test conditions, test results, and discussion of the testing program are presented.

4.2 OBJECTIVE

The purpose of this testing program was to evaluate the thermal stability of the organic components of cementitious materials which had been formulated with organic-based superplasticizers. By utilizing mass spectroscopy and examining the gases released during the thermal processing of the paste samples, the presence or absence of CO₂ could be correlated with the thermal decomposition of the organic superplasticizer subjected to temperatures up to 300°C, which is 100°C higher than the maximum allowable drift wall temperature. Running the test to

higher than expected temperatures would increase the chance of discovering any changes in the organics.

4.3 TEST MATRIX

Two types of superplasticizers were used in the tests: 1) Rheobuild 1000, a naphthalene-based superplasticizer, with a long-term history of use in the construction industry, and 2) ADVA, a new proprietary carboxylated polyether superplasticizer. In order to investigate the evolution of the organic admixtures in the hydrated cement paste, the acceleration of the above processes in the laboratory time scale was necessary, hence, crushed cement paste samples were employed because they have higher surface areas exposed and thus the reaction rates are increased.

The tests were designed to determine the following: 1) evolution of gases (especially CO₂ gas) from hydrated cement paste in specified conditions, 2) measurement of pH of each specimen before and after testing and monitoring of any change in pH, 3) compressive strengths of the different formulations at different ages, and 4) characterization of mineral compositions of all samples by x-ray diffraction and scanning electron microscopy at all ages.

Paste specimens were formulated so that they reflected the general proportions of potential concrete formulations without the coarse and fine aggregates, that is: Type II portland cement, silica fume, water, and superplasticizer. It should be noted that Type V cement was proposed for the concrete mix design (see Table 3 in Sec. 5.3.1). However, Type II cement was selected in the test program. The reason is that to have proper workability smaller amounts of superplasticizers are needed for Type V cement than for Type II due to its lower C₃A content (Ref. 8.3). Since the major purpose of this test program is to determine the evolution of organic admixture, i.e., superplasticizer in the cement, use of Type II cement would give a more conservative result. Table 1 summarizes the formulations based upon the designated superplasticizer Rheobuild 1000. These variations reflect differences in the silica fume to cement ratios. All formulations were developed with approximately 4% by weight of liquid superplasticizer to cementitious components. This concentration reflects dosages at the maximum level and was selected to allow for the best possible identification of decomposition products of the organic portion if they evolved.

4.4 TEST CONDITIONS

Evolution of organic admixtures in cement pastes was examined using the samples prepared with the following test conditions:

- A) Control samples were prepared without addition of silica fume and superplasticizer.
- B) Test samples were prepared with the following test parameters:

Silica fume content: 10 to 30% by weight of cementitious material

Table 1. Formulations of Tested Specimens (% by weight)

	TRW-1	TRW-2	TRW-3*	TRW-5**
Type II Cement	68.70	56.00	53.44	66.16
Silica Fume	7.60	24.00	22.90	7.32
Water	20.60	16.80	20.61	23.52
Rheobuild 1000	3.10	3.20	3.05	3.00
water/cementitious solids	0.27	0.21	0.27	0.32
silica fume/cementitious materials ratio	0.10	0.30	0.30	0.10
superplasticizer/ cementitious materials ratio	0.041	0.04	0.04	0.041

* This mixture is similar to mixture TRW-2 except that the water content is higher and equals that of Mixture TRW-1 [water/(cement+silica fume) = 0.27].

** This mixture is similar to mixture TRW-1 except that the water content is higher [water/(cement+silica fume) = 0.32].

Superplasticizer content: approximately 4% by weight of cementitious material
 Water/cementitious material ratio: between 0.2 and 0.4
 Curing condition: stored in sealed containers at nearly saturated relative humidity at 38°C for a minimum of 14 days and followed by crushing and exposure to CO₂-free dry air at < 30% relative humidity for additional 14 days
 Temperature for gas evolution test: 100, 200, and 300°C
 Duration of gas evolution test: 1, 3, 7, 14, and 28 days

The particle size requirements for the crushed cement-paste samples was No.4 sieve size or finer for most samples except for samples TRW-5 at 7, 14, and 28 days for which particle sizes were smaller than No. 30 sieve in order to be suitable for D-drying. The gases developed were monitored as a function of time at each specified temperature. At least one control batch of samples was tested for each test condition.

4.5 TEST RESULTS

The pH values of pore fluids expressed from the samples for the different formulations at

different ages are shown in Table 2. Note that due to the high silica fume content and low water/cementitious material ratio of the sample TRW-2, no pore fluid was collected for pH measurement. All pH values are generally lower than those of normal cement pastes without silica fume which are controlled by the alkali from the cement and have a value of approximately 13.5. These values indicate a greater extent of consumption of alkalis by silica fume and more nearly approach the values established by $\text{Ca}(\text{OH})_2$ of 12.4. However, it should be noted that these are pH values determined for normal temperature curing, and do not reflect the lower pH values characteristic of high temperature curing of silica-rich concrete compositions (Ref. 8.4).

Table 2. pH Values of Cement Pore Fluids at Different Ages

	TRW-1	TRW-2	TRW-3	TRW-5
1 Day	n/a	n/a	12.70	12.60
3 Days	n/a	n/a	12.60	12.67
7 Days	12.60	n/a	12.60	12.72
14 Days	12.90	n/a	12.60	12.70
28 Days	n/a	n/a	n/a	n/a

n/a - Could not obtain pore solutions.

Powder x-ray diffraction (XRD) was used to identify the mineralogical phases. The x-ray diffraction patterns for specimens at different ages were measured for formulations TRW-1 and TRW-3. Figs. 1 and 2 show typical x-ray diffraction patterns for samples TRW-1 and TRW-3, respectively. The results of x-ray diffraction analysis indicate that TRW-1 contains portlandite up to 28 days, while sample TRW-3 no longer contains portlandite at 7 days and beyond, reflecting the higher silica fume content. The C-S-H (major hydration product of cement) appears to be in a gel form. It appears that the hydration reaction is not yet completed at 28 days of age as shown by the presence of the residual alite.

The results of gas evolution tests on all the Rheobuild superplasticizer-containing cement paste samples (either freeze-dried or D-dried) indicate that no carbon dioxide was observed at temperatures up to 300°C. Fig. 3 shows a typical result of mass spectroscopy of a freeze-dried sample (obtained for TRW-1 after curing for 28 days). Fig. 4 shows the result of mass spectroscopy of a D-dried sample of TRW-5 after curing of 28 days, in which a mixture of ~20% oxygen and 80% nitrogen was passed through the sample.

The failure to observe any carbon dioxide in the off gas emissions of any of these tests does not support the initial postulate of this study (see Sec. 4.1). Two possible scenarios could account

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TIME: 21:31

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STEP: 0.020

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WL: 1.64059

Fig. 1 X-ray diffraction pattern of the sample TRW-1 at 28 day.

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TIME: 21: 31

PT: 0.600

STEP: 0.020

SCINTAG/USA
WL: 1.54059

Fig. 2 X-ray diffraction pattern of the sample TRW-3 at 28 day.

Fig. 3 Results of mass spectroscopy of a freeze-dried sample of TRW-1 after curing for 28 days.

Fig. 4 Results of mass spectroscopy of a D-dried sample of TRW-5 after curing for 28 days. The test was conducted with a mixture of ~20% oxygen and 80% nitrogen flowing through the sample.

for the observations in these studies: 1) the superplasticizer is stable at the temperatures of the study, and 2) the superplasticizer decomposes and produces predominantly carbon dioxide and water which would react with the calcium hydroxide or dehydrated calcium silicates to form calcium carbonate and not be observed in the off-gas atmosphere.

However, since the test results of evolution of the dehydrated superplasticizer itself under the conditions of the experiment also did not indicate release of any carbon dioxide, as shown by Fig. 5, i.e., the scenario 2 above does not exist. It is concluded that the superplasticizer dispersed onto the cement paste system is stable and will not release carbon dioxide under the experimental conditions.

4.6 EXPERIMENTAL MODIFICATION AND TEST RESULT DISCUSSION

During the course of this testing program, recommendations were made with regard to the experimental design that was implemented. The initial design of the gas evolution apparatus had the paste sample heated under a vacuum. This condition could cause the decomposition of the organic superplasticizer in the presence of a reduced oxygen fugacity and as such may result in charring of the superplasticizer rather than decomposition into carbon dioxide. To address these concerns, the system was modified so that both a mixture of gases (nitrogen and oxygen only) and a dry, medical air with an ascarite carbon dioxide scrubber were introduced into the reaction zone at test temperatures. The pressure of the inflowing gas mixtures instead of the vacuum pump flushed the gases from the system and past the mass spectrometer intake. It should also be pointed out that the drying method for the samples for gas evolution test was modified during the course of the study. The freeze-drying method was used for samples TRW-1 and TRW-3. Because of concerns that freeze-drying could impact the behavior of the paste, the procedure of drying was modified with sample TRW-5. Samples at 1 and 3 days were freeze-dried as normal; then the drying methodology was modified, and the remaining samples of TRW-5 at 7, 14 and 28 days were D-dried.

The reason for the above mentioned modifications was to make sure the gas evolution test for these cement samples was conducted in an adequate and satisfactory manner such that if there was any evolution of carbon dioxide due to the decomposition of the superplasticizer under test condition, it could be monitored and measured. Nevertheless, as was pointed out in the previous section, no carbon dioxide was observed from gas evolution tests on cement samples containing the Rheobuild superplasticizer and superplasticizer itself. These results lead to the conclusion that naphthalene-based superplasticizers within the cement samples will not be decomposed under dry condition at temperatures up to 300°C.

Fig. 5 Results of mass spectroscopy of Rheobuild 1000.

Another study by Feylessoufi et al. (Ref. 8.12, p. 25) indicated that thermal decomposition of the melamine-based superplasticizer in vacuum does not begin until after 300°C. Note that most of the commercial superplasticizers used in concrete are either naphthalene- or melamine-based. Dr. Onofrei (Ref. 8.13) indicated that superplasticizer with lower molecular weight (or with short chain) may decompose first. Khorami and Aitcin's (Ref. 8.14, p. 117) investigation of six different commercial superplasticizers (including five naphthalene- and one melamine-based) indicated that thermal degradation for the polymeric material occurs between about 280 and 600°C in N₂-gas environment, with lower temperatures (280 to 450°C) for melamine-based and higher temperatures (mostly > 440°C) for naphthalene-based superplasticizers.

Based on the above discussion, it may be concluded that the superplasticizers used for concrete lining will not decompose under prolonged exposure to elevated temperatures (up to 200°C) in the dry emplacement drift environment. Also, due to the absence of carbon dioxide, carbonation of the concrete due to thermal decomposition of superplasticizers is not expected to occur in this situation. Note that carbonation of concrete due to air in the drifts may occur, this process was not part of this study.

It should also be pointed out that all the above mentioned tests were performed over a short periods. The concrete lining for the emplacement drifts has a planned operation life of 150 years. Although the time frame is quite different, it appears that the conclusion from this short-term testing program is valid for longer periods, because superplasticizers do not alter fundamentally the structure of hydrated cement paste. Their function to improve the concrete workability occurs within the first few hours after mixing (see Sec. 6.2). Nevertheless, it may be worthwhile to conduct additional gas evolution tests for longer periods, say 3 months to half a year. If the results for these longer periods still do not change, it will help to confirm the above conclusion.

5. ASSESSMENT OF ALKALINITY IN CEMENTITIOUS REPOSITORY

5.1 INTRODUCTION

Portland cement concretes have been in increasing use for about 150 years, and it might be supposed that their properties are well established. Many of the most relevant mechanical properties with respect to civil engineering are, indeed, well-established: for example, compressive and flexural strength, creep, fatigue, compatibility with other engineering materials such as steel, and performance in a corrosive environment, all are well documented (Ref. 8.15). But the chemical as well as mechanical performance of concrete in a radioactive waste repository will require more extensive testing than that for concrete in a conventional environment due to the long-term exposure to elevated temperatures.

There are many factors involved in the chemical behavior of cement performance, such as pH, Eh, solubility, sorption, etc. Among which, perhaps the single most important factor is pH (Ref. 8.15). The pH value of concrete can be reduced by the addition of pozzolans such as silica fume. Adding silica fume can also increase the strength of concrete. However, there is one negative influence associated with the addition of silica fume, which is the decrease of the cement fluidity. Although this problem usually can be solved by adding organic admixtures to the cement, the potential postclosure performance resulting from the organic materials requires further investigation.

Based on the current evaluation of cementitious material from Performance Assessment (Ref. 8.5), a target pH value of about 10 or lower is desirable from the postclosure performance viewpoint. It should be noted that this value is a preliminary recommendation. Furthermore, a concrete with a cement paste pH value of 10 is difficult to achieve by the addition of silica fume alone. Even with 30 percent of silica fume, the pH value of the cement pore solution will not drop below 11.5 (Ref. 8.24).

Because the use of silica fume aids in reducing the potential pH of the concrete system, two concrete mix design options incorporating different amounts of silica fume are considered to help in understanding how to achieve this goal. One option would contain a moderate amount of silica with a normal proportion of concrete mix with 10 to 20 percent of silica fume by weight, and another option would contain a relatively high amount of silica, in the form of silica fume and silica flour, and require a little more superplasticizer. Development of these options is discussed in the following sections (see Secs. 5.3.1 and 5.3.2).

5.2 CHEMICAL NATURE OF CEMENT

In order to assess the impact of cement alkalinity on the long-term geochemical behavior of the repository, it is essential to understand the chemical behavior of cement.

5.2.1 CHEMISTRY OF HYDRATION

Portland cement is a complex mixture of four major principal compounds: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). They make up 90% or more of the weight of portland cement (Ref. 8.6, p. 3). The reaction of portland cement with water, called hydration, leads to the setting and hardening of the cement. All the compounds present in the portland cement clinker are anhydrous, but when brought into contact with water they are all attacked or decomposed, forming hydrated compounds (Ref. 8.16) with the rate of hydration decreasing in the following approximate order: $C_3A > C_3S > C_4AF > C_2S$. The hydration of C_3S is primarily responsible for the early strength of the cement-water system. C_3A also plays an important role in the early setting behavior of cement due to its rapid reaction with water. Superplasticizers principally affect the rheology (flow characteristics) of water-cement mixtures for the first few hours after mixing (Ref. 8.17).

Hydration begins as soon as cement comes in contact with water and will continue as long as space for hydration products is available and moisture and temperature conditions are favorable. As hydration continues concrete becomes harder and stronger. Most of the hydration and strength development take place within the first month of concrete's life cycle, but they continue, though more slowly, for a long time; strength increases over a 50-year period have been recorded in laboratory investigations (Ref. 8.6).

The normal hydration products of cement include two major phases in the $CaO-SiO_2-H_2O$ system: a $Ca(OH)_2$ phase and a phase called calcium silicate hydrogel (i.e., C-S-H gel) with a variable Ca/Si ratio (Ref. 8.18), normally at ~ 1.7 but as low as 0.9 in silicious-blended cements (Ref. 8.15). Other phases, e.g., aluminoferrite and aluminosulphates may also form, but are quantitatively less important (Ref. 8.18). $Ca(OH)_2$ is largely crystalline and is isostructural with the naturally occurring mineral, portlandite. On the other hand, the C-S-H phase is nearly amorphous, the particles of which are so minute (less than $1\ \mu m$) (Ref. 8.19) that they can be seen only under an electron microscope, yet it is the most important cementing component in concrete (Refs. 8.20, 8.6). It is generally accepted that it is this system which dominates the composition of the pore fluid in cement, particularly with regard to pH control (Ref. 8.21). It should be noted that although C-S-H gel is almost amorphous, it could gradually crystallize over a very long time scale. Since the crystalline materials are more stable than the gels, they would have lower solubility in water and establish lower pH (Ref. 8.21). Moreover, the pH of the C-S-H system declines as the Ca/Si ratio decreases (Ref. 8.15). The partial crystallization of the C-S-H system is described in Sec. 5.2.3.

5.2.2 ANALYSIS OF THE CEMENT PORE FLUID

In order to assess the alkalinity of the cement paste pore water, it is necessary to have an adequate understanding of the chemical evolution of the cement pore fluid. An analysis of the

compositions of cement pore fluids by Glasser et al. (Ref. 8.20) discloses the following points:

1. The pore fluid consists mainly of Na^+ and K^+ with OH^- as the counter ion; Ca^{2+} is insoluble and the solubility of Mg, Al, Si, Fe, and SO_4^{2-} remains generally low.
2. Other things being equal, alkali concentrations are a function of the total alkali content of the cement; high alkali cements give rise to more alkaline pore fluids.
3. High W/C ratios tend to dilute the alkali.
4. Much of the alkali present in clinker is released rapidly to the pore fluid.
5. Pozzolanic materials, especially silica fume, depress pore fluid alkali contents.

It should be noted that with respect to sodium distributions, much of the sodium is retained by the solid phases; for ordinary portland cement, only about 25% of its total Na is released to the pore fluid. Compared with other pozzolans such as fly ash and blast furnace slag, silica fume has a marked improvement in the capacity of the solid phases to retain sodium. On the other hand, much less of the potassium is retained by the solid phases. In ordinary portland cement, about 70% of the potentially-available potassium is in the pore fluid. Silica fume again can give the drastic removal of K, only about 20% of which is found in the pore fluid (Ref. 8.20). The effect of adding silica fume to reduce the pH of the cement is further discussed in Section 5.3.

It should be pointed out that not just the alkali content influences the pH of the cement, the cement content itself also affects the pH value. The lesser cement content will lower the pH, but not in direct proportion. This concept is applied to the high-silica concrete mix design in Section 5.3.2, in which cement content less than that in normal concrete (usually with cement content greater than 300 kg/m^3) is proposed.

5.2.3 EFFECT OF ELEVATED TEMPERATURES

It is expected that the emplacement drifts will be subjected to elevated temperatures (i.e., >100 to 200°C) after waste emplacement for an extended period of time (at least thousands of years). The cementitious materials composing the concrete lining will be subjected to the same temperature as the surrounding host rock. The majority of studies of cement phase behavior have been limited to the $20\text{--}25^\circ\text{C}$ range. Very little research has been conducted on the chemical behavior of cement subjected to prolonged high temperature exposure. Atkins et al. (Refs. 8.15, 8.22) investigated the cement phase chemical behavior under temperatures ranging between 25 to 100°C . Their investigations on the C-S-H system have shown that partial crystallization can occur at a relatively low temperature (55°C) within a few months. The rate of crystallization decreases with increasing Ca/Si ratio. These observations were supported by observations on blended cements after prolonged cure at $80\text{--}100^\circ\text{C}$ (Ref. 8.22). Due to the partial crystallization process, the intrinsic solubilities in the C-S-H system are depressed and buffer pH at a lower value.

In another study by Atkins et al. (Ref. 8.15), phases in the C-S-H system were prepared by

adding appropriate amounts of CaO and silicic acid, to give Ca/Si ratio of 0.9, 1.3, and 1.7, to degassed/distilled water and sealed in polyethylene containers. Samples were cured at 25, 55, and 85 °C for up to 200 days to test their thermal stability. Results of X-ray investigation of the phase evolution showed that C-S-H gel can persist to about 60 °C, except at Ca/Si ratio of 0.9, where partial crystallization occurred, giving rise to C-S-H I (poorly crystallized foils or plates with a tobermorite-like structure). At 85 °C, crystallization is more complete at all ratios, with tobermorite formed at Ca/Si of 0.9, and jennite for two higher Ca/Si ratios.

One principal finding from the study by Atkins et al. is that since C-S-H is unlikely to persist in brief (200 days) exposure to elevated temperature, it will probably not persist in much longer time under higher temperature. However, for the emplacement drift situation, the C-S-H phase may not be completely crystallized under dry condition, which is different from the hydrothermal condition in Atkins et al.'s experiment, but may eventually transfer to more stable crystalline phase with time under elevated temperature. Since the temperature at emplacement drifts will be higher than 85 °C for a prolonged period (up to thousands of years), the crystallization of C-S-H gel will probably be complete and reduce the pH and the capacity of concrete to maintain a high pH.

5.3 ALKALINITY OF CEMENT IN THE REPOSITORY

Fresh normal portland cement paste has a very high alkalinity. A high-alkali cement leads to a pH of between 13.5 and 13.9, while a low-alkali cement results in a pH of 12.7 to 13.1 (Ref. 8.23, p. 518). The pH at the repository is expected to decrease from these values due to the following factors: 1) crystallization of C-S-H gel at elevated temperature, 2) leaching due to water seeping through the repository, 3) decalcification of hydrated cement phase (especially C-S-H gels) from the carbonation, and 4) decrease of Ca/Si ratio by adding silica fume. The first factor has been discussed in the previous sections. The second factor regarding water leaching the cement is not within the scope of this study. In the current repository design, the repository block is at 100 m above the groundwater table (Ref. 8.7). Unless the repository reflux situation changes or inflow from perched water or surface runoff occurs, a scenario of a large amount of water contacting the cement does not exist. The third factor regarding carbonation due to air in the drift is not within the scope of this study. The fourth factor is one of the major measures in concrete mix design that can be utilized to reduce the pH values, i.e., to add silica fume, and will be discussed in the following sections.

5.3.1 MODERATE-SILICA CONCRETE

For this option, a concrete mixture using 15 percent silica fume by weight of cement is developed. The detailed procedure for proportioning components are described in an M&O report "Materials for Emplacement Drift Ground Support" (Ref. 8.11). For this study, only the summary of the preliminary composition of the concrete mix design (Ref. 8.11) is shown in Table 3. Note that there has been minor modification compared to Table 7.5 of Ref. 8.11. As can

Table 3. Preliminary Mix Design for Moderate- and High-Silica Concrete

Component	Moderate-Silica Mix (kg/m ³)		High-Silica Mix (kg/m ³)	
	Type V portland cement	398	Type V portland cement	200
Water (to be added)	W/C=0.4	160	W/CM=0.5	118
Coarse aggregate	19 mm (3/4") max. size*	1003	13 mm (1/2") max. size	1003
Fine aggregate		777		816
Silica fume	15% of cement wt.	59	50% of cement wt.	100
Silica flour (inert filler)	None	0	<50 micron size	185
Superplasticizer	1.75% of cemen. material	8	3% of cemen. material	9

Note: This mix design is intended for the manufacture of precast concrete. For cast-in-place mix design, change the maximum coarse aggregate size to 1/2 in. and adjust the volume of coarse and fine aggregate to increase the workability.

be seen in Table 3, water reducer is not included and the dosage of superplasticizer is increased a little. The reason for this is to reduce the number of additives as a means of decreasing the chemical complexity for long-term performance. In addition, lesser superplasticizer is required to achieve the same desired workability.

The influence of silica fume on the pH of the solution has been studied to assess the corrosion potential. The plain cement paste shows a pH of about 13.5. Addition of silica fume results in a progressive decrease in pH by consuming the available $\text{Ca}(\text{OH})_2$. A corresponding reduction in the total available alkali metal cations in solution is also observed. However, at an addition of 10 to 20% silica fume the pH value does not drop below that of a saturated $\text{Ca}(\text{OH})_2$ solution which is approximately 12.5 (Ref. 8.9). Even at 30% silica fume, the pH does not drop below 11.5, which is considered to be a threshold value for maintaining a good passivity of embedded steel in concrete (Ref. 8.24). It should be pointed out that these pH values are mainly for "young" cement pastes compared with 150 years of operational life of the repository. Also, it should be noted that the steel fiber reinforced (not steel-rebar reinforced) concrete is preliminarily designed for the concrete lining at the crown and sidewall portions at this time (Ref. 8.11). If it is found necessary to have steel rebar in these portions of concrete lining in the final design, further investigation about the pH value of cement paste is needed. Furthermore, there are other actions that may reduce pH values in the cement paste solution during the postclosure period: microbial activity, the oxidation of carbon steel from the waste package, radiation effect on water chemistry, and the carbonation effect. Although there are some uncertainties regarding these in reducing pH, it appears reasonable to take them into consideration. For example, even though the starting pH value of the cement paste solution may be above 10, the long-term pH value during the postclosure period might be expected to drop due to those potential actions mentioned above.

With this option of concrete mix design, not only the strength requirement for concrete lining in emplacement drifts subjecting to temperatures up to 200°C can be met, the permeability of the concrete will also be very low, a desirable factor for long-term durability. However, if the long-term pH value during the postclosure period is not low enough to meet the PA requirement, then concrete supports may not be acceptable (Ref. 8.31, CDA: DCSS 034).

5.3.2 HIGH-SILICA CONCRETE

For this option, a concrete mix with a low-quantity cement content, a larger amount of silica fume and silica flour, and a higher dosage of superplasticizer is proposed. The concept of this mix design is based on a Low-Heat-High-Performance Concrete (LHHP), which was developed by AECL-WL Canada for high mass structures that are being proposed for use in the geological isolation and disposal of radioactive wastes in Canada (Ref. 8.5). One of the advantages in this concrete is that it has a low pH values in the range of 7.8 to 9.5, which is mainly attributed to the very low cement content (97 kg/m^3) and large amount of silica fume (97 kg/m^3).

Since the target pH value in the proposed concrete mix design is lower than 10 for the post-closure period, the amount of cement content may not need to be as low as that of LHHPC. Also, the silica fume percentage is selected to be 50% instead of 100% of the cement by weight (see mix design in Table 3). Due to the low quantity of cement and large amount of silica fume in this mix design compared with normal portland cement concrete, the resulting pH value of the cement paste solution could be much lower than 12.5, but will not be as low as that of LHHPC, i.e., 7.8 to 9.5. It is expected to be below 10. The actual pH values will not be known until the trial mixes are prepared and samples tested. Currently, a testing program is scheduled to start testing mechanical properties and measuring pH values of concrete specimens for both moderate- and high-silica concrete mix designs at elevated temperatures in the summer of 1998. If the test results show that the pH value is above 10, then the concrete mix design will be modified and further tests may need to be done. The pH results may provide some insight on whether the pH can be lower than 10 even though the age of the tested concrete is quite young compared with 150-yr concrete lining to be placed in the repository environment.

5.4 IMPACTS OF CONCRETE ALKALINITY ON WASTE ISOLATION

The postclosure evolution (i.e., change of properties with time) of cementitious materials in the repository emplacement drifts has potential detrimental effects on waste isolation due to the alkalinity of the concrete. Potentially harmful effects are:

(1) Radionuclide transport

Concrete pore solutions with high pH have the potential to increase radionuclide solubility limits via CO_3^{2-} and OH^- complexing, of which the major concern is the potential effects on dissolved actinide concentrations (Np, Pu, Am). Colloids generated from cementitious materials may also sorb radionuclides and could enhance transport if they migrate in groundwater. Alternatively, certain cement solids (i.e., C-S-H phases) and possible alteration minerals of cement may provide both sorption and cation exchange sites for radionuclides, thus providing some level of retardation. However, the potential radionuclide transport mechanism is considered the dominant mechanism and is of primary concern (Ref. 8.5).

(2) Natural barrier sorption

Constituents dissolved from concrete, such as hydroxide and carbonate, form negatively charged complexes with metal cations, such as uranyl ions. Such complexes have low or non-existent capability to adsorb onto the negatively charged rock surface and thus could reduce or eliminate sorption of radionuclides by natural barrier components such as zeolites.

(3) Production of water

Water from dehydration reactions within the cement could be produced in the near-field environment and possibly increase the relative humidity. The amount of water added to the near-field environment can be minimized by using precast concrete instead of cast-in-place, which would reduce free water by the curing/hydration of cement paste and encourage water migration out of the cement before placement of the lining. Thus, this should not be a major effect.

(4) Changes in rock mass porosity and permeability

The porosity and permeability of the host rock could be changed by increases in silica solubility. Silica (for example, quartz and amorphous silica) solubility increases above a pH value of 10 (Ref. 8.5). Silica minerals are about 79% of the repository host horizon (see Table 4.1 of Ref. 8.11) and formation of alteration phases could change porosity and permeability. The extent to which this would occur and the potential performance consequences are uncertain.

Preliminary recommendations from PA, based on consultation with cement consultants, do not preclude the use of concrete but emphasize the need to minimize potential impacts on the repository from the use of concrete, as follows (Ref. 8.5):

If concrete is desirable to use as lining for ground support, then minimizing the potential postclosure impacts on the waste isolation capabilities of the site will most likely be achieved by (a) using precast concrete, (b) designing a mix with lower Ca/Si ratio, (c) using techniques such as particle size engineering, steam-curing, or pressure-curing to reduce the concrete permeability and water content needed for higher silica cements, (d) using tuff aggregate, and (e) investigating alternative cements, such as C_2S cement, that may have a lower pH than standard portland cements.

These recommendations and other aspects of long-term material performance were considered in the M&O report "Materials for Emplacement Drift Ground Support" (Ref. 8.11).

6. EVALUATION OF ORGANIC MATERIALS

6.1 INTRODUCTION

The introduction of organic materials into the emplacement drift area may have an impact on performance through changes in the concentrations of organic acids and organic colloids which can increase waste package corrosion, radionuclide solubility and transport, and silicate mineral dissolution. In addition, organics may promote microbial activity which is another factor leading to waste package corrosion. Furthermore, organic substances can take part in oxidation/reduction reactions and may contribute to the generation of locally reducing conditions (Ref. 8.8).

For the current study, a moderate to large amount of silica fume is proposed to reduce the pH value of the cement paste solution which, in turn, indicates a need to use a great amount of superplasticizer to achieve the proper workability. Since all the current commercial superplasticizers are organic materials, the addition of superplasticizer will probably introduce organic materials into the repository drift environment. In order for these materials to be considered acceptable from the postclosure performance viewpoint, adequate knowledge of their chemical nature, composition and quantities (mainly the solid portion in the liquid) are necessary.

6.2 FUNCTION OF SUPERPLASTICIZERS

The major role of organic superplasticizing admixtures is to achieve water-reduction and promote increased fluidity or workability in cement paste and concrete mixtures. In addition to improving the workability of concrete at a given water/cementitious material ratio, superplasticizers provide a number of other technical benefits such as: a) production of a hydrated cement paste, stable and dense enough to bond strongly to aggregates and produce a very strong composite material, b) production of a concrete with very low porosity and permeability, and c) significant increase in the density and durability of concrete, giving a greater resistance to the penetration of aggressive agents and an improved service life (Ref. 8.13).

Superplasticizers are an essential component of silica fume-containing concretes, in particular, because of the very high surface area of the silica fume, which substantially increases the water requirement of the concrete. There are three principal types of superplasticizers: 1) lignosulfonate-based, 2) polycondensate of formaldehyde and melamine sulfonate (often referred to simply as melamine sulfonate), and 3) polycondensate of formaldehyde and naphthalene sulfonate (often referred to as naphthalene sulfonate) (Refs. 8.6 and 8.24). A number of newer types of superplasticizers including carboxylated polyethers (e.g., ADVA) appear to have significantly different functions in the slurries and may be used in smaller proportions to increase fluidity, but are not yet widely used in practice.

Among these three major types of superplasticizers, lignosulfonate superplasticizers are generally used in conjunction with either melamine or naphthalene superplasticizers when high strength concrete is desired. Naphthalene superplasticizers have been in use longer than any of the others, and are available under a number of brand names. They are generally available as either calcium salts, or more commonly, sodium salts. The particular advantages of naphthalene superplasticizers, apart from their being slightly less expensive than the other types, appears to be that they make it easier to control the rheological properties of high strength concrete because of their slight retarding action (Ref. 8.24).

Superplasticizers do not alter fundamentally the structure of hydrated cement paste. The main action of superplasticizers is to wrap themselves around the cement particles and give them a highly negative charge so that they repel each other. This results in deflocculation and dispersion of cement particles, which improves the concrete workability (Ref. 8.23). The magnitude of this dispersing effect generally increases with increasing molecular weight of the polymer. Some carboxylated polyethers, in contrast, are less adsorbed by the cement particles and appear to achieve their superplasticizing effect dominantly by steric hindrance rather than simple electrostatic repulsion.

Superplasticizers affect the rheology of water-cement mixtures for the first few hours after mixing. It is suggested that they may interfere with the fastest hydration reactions. Onofrei's adsorption study of naphthalene-based superplasticizers indicates that the majority of adsorbed superplasticizer resides within the C-A-H and calcium-rich C-S-H phases after hardening has occurred, in which the latter phase is C_3S hydrate while the major constituent in the former phase is C_3A (Ref. 8.3).

6.3 ORGANIC ADMIXTURES IN CONCRETE

In this section, the amounts of organic materials to be used in concrete lining for ground support in emplacement drifts are described. Only organic materials from the superplasticizers in both moderate- and high-silica options are considered.

As discussed in Sec. 7.4.5 of Ref. 8.11, water-reducing admixtures are used to reduce the quantity of mixing water required to produce concrete of a certain slump, reduce water-cement ratio, or increase slump. High-range water reducers (also called superplasticizers) conforming to ASTM C494 (Ref. 8.25) Type F or G generally reduce water content by 12% to 30% (Ref. 8.6). Superplasticizers are often used to produce flowing concrete with slumps about 7-1/2 in. (19 cm) or more, with no increase in water demand other than that contained in the admixture based on ACI 211.1 (Ref. 8.26).

In the following two subsections, quantity and type of superplasticizers which are proposed to be used in the repository ground support concrete lining are presented. It should be noted that the estimated quantity of organic material is preliminary; the exact quantity will not

be known until the final mix designs have been approved and trial mixes have been completed.

6.3.1 MODERATE-SILICA CONCRETE

Based on Table 3 of Section 5.3, the required superplasticizer for moderate-silica concrete mix design is 8 kg/m^3 . The volume per linear meter of concrete lining is 3.85 m^3 (see p. 58 of Ref. 8.11). It is noted that the calculated concrete volume is only an estimate based on configuration of a 5.5-m emplacement drift with 20-cm lining thickness as shown in Figure 7.5 of Ref. 8.11. It includes the volume of lining and invert but not the pier above the invert. It should also be pointed out that the amount of high-range water reducers used in the mix design is based on Rheobuild 1000 superplasticizer. Rheobuild 1000 is a very popular commercial superplasticizer, which is an aqueous solution of sulfonated naphthalene superplasticizer (Ref. 8.11). It is of liquid type with solid amounts in the range of 38.5 to 42.5% of the total masses (Ref. 8.27). Theoretically speaking, only the amount of these solid materials, rather than the total mass, should be considered as organic materials.

6.3.2 HIGH-SILICA CONCRETE

In this option, superplasticizer amount is 9 kg/m^3 based on dosage for Rheobuild 1000, as shown in Table 3. As indicated in the foregoing section, the solid portion is about 40.5% (average), i.e., about 3.65 kg per cubic meter of cementitious material. Very recently, a new commercial product of superplasticizer with a name of Rheobuild 3000 FC (also called PS-1140) was developed. It is said that only about half of the dosage as that of Rheobuild 1000 is needed to produce the same workability (Ref. 8.28). Moreover, the solid content of this new product is 27.0 to 33.0% of the total mass, which is about 25% less than that of Rheobuild 1000. From an organic material quantity viewpoint, this new product is desirable because its total available solid content of organic material is about 37% of that of the former. Yet, it should be noted that since it is a new product with a different chemistry (not a naphthalene-based superplasticizer), its compatibility with cement and other chemical behavior needs to be further investigated.

6.4 ORGANIC MATERIALS FROM OTHER SOURCES

Although it is now certain that superplasticizers in concrete will increase the total organic materials in the repository, the significance of this increase can only be judged when realistic assessment of the quantity and type of organic materials from other sources in the repository are available. It is not within the scope of work to quantify and locate the organic material from other sources in this study. The intention here is to provide some background information to identify such materials.

In general, these sources can be grouped into two categories: 1) naturally occurred, and 2) introduced (or man-made). The introduced organic materials mainly come from ESF

construction, construction and development of repository, waste emplacement operation, and backfilling.

1. Naturally occurred

- from ground water
- from soil zone on the surface

2. Introduced (or man-made)

1) ESF construction

- wood lagging, cribbing, and blocking
- cementitious materials for shotcrete
- rubber from invert gaskets, conveyor belts and electric cables
- lubricants, hydraulic fluids, and coolants from TBM and diesel equipment
- diesel exhaust from locomotives and other diesel equipment
- water for dust control, clean up, and excavation
- residues from drilling and blasting

2) Construction and development of the repository

- basically same items as those for ESF construction

3) Waste emplacement operation

- rubber from electric cables
- lubricants, hydraulic fluids, and coolants from diesel equipment

4) Backfilling

- backfill material, such as tuff stored on surface with long time exposure to atmospheric conditions, especially rain and organic materials accumulated on it; or clay used for backfill.

The above list may not cover all potential organic materials from other sources but it does demonstrate the types of materials that may be found in the repository.

6.5 ASSESSMENT OF POTENTIAL USE OF SUPERPLASTICIZERS BY BACTERIA

One of the major concerns about superplasticizers in concrete lining is that they may be used as a nutrient supply for bacteria growth. A recent preliminary result of Stroes-Gascoyne's research on "Biodegradation of a Superplasticizer, Sodium Sulphonated Naphthalene Formaldehyde Condensate by Bacteria Naturally Present in Granitic Groundwater" (Ref. 8.29) may provide some insight on this subject. The experimental results indicate that incubation of Underground

Research Laboratory (URL) (in Canada) groundwater bacteria with Disal (a naphthalene-based superplasticizer) did not result in a significant increase in cell numbers ($< \text{factor } 3$) even with additions of NaNO_3 , K_2HPO_4 , or both, with two exceptions. Besides, Disal concentrations after 47 days did not show conclusively that degradation has taken place. A number of factors may have influenced the results, which include: lack of adaptation time (47 days may have been too short); Disal concentrations too high (toxic effects?); bacteria present could not break down the polymer into monomers. It should also be noted that the incubation for the experiment is under temperatures of 10 and 30°C, which are much different from the conditions in repository environment such as elevated temperature and radiation-affected condition.

Based on Stroes-Gascoyne's viewpoint, superplasticizers (especially long-chain) will probably not be used as nutrients for bacteria under repository conditions. However, she emphasized that the microbial effect is gradual; there is no 'black and white' answer, which depends on many environmental factors. It is expected that maintenance of hot ($>120^\circ\text{C}$) and dry condition for an extended period will probably prevent all biotic activity in affected areas (Ref. 8.30). To confirm this point, it seems desirable to perform similar tests using cement paste samples containing various superplasticizers subjecting to low and high temperatures for longer periods, e.g., three months or longer. The reason of using cement paste samples containing superplasticizers instead of just superplasticizers along is that the nature of superplasticizers in concrete may be very different from superplasticizers not reacted with the cement mix in terms of the molecular structure, chemical reactivity, etc.

Results of the assessment on potential use by bacteria provide important insight regarding the effect of organic materials on waste package isolation, i.e., the organic admixtures from superplasticizers in concrete will probably not be used by microbial activity. However, as described in Sec. 6.1, there may be some other detrimental effects caused by organic materials. Moreover, there are some other sources of organic materials, as indicated in Sec. 6.4, in the repository environment, of which further study needs to be done to determine their amounts and impacts on the postclosure performance.

7. CONCLUSIONS AND RECOMMENDATIONS

The results of gas evolution tests on all the Rheobuild superplasticizer-containing cement paste samples indicate that no carbon dioxide was released at temperatures up to 300°C. The failure to observe any carbon dioxide in the off gas emissions of any of these tests does not support the initial postulation of this study, i.e., under the dry and elevated temperature environment, the organic admixtures in the concrete will be decomposed and volatilized as gases, mostly CO₂ with other minor components such as SO₂ and NO_x.

Based on the results of gas evolution tests on cement paste samples which include naphthalene-based superplasticizers and on superplasticizers alone (which include naphthalene-based and carboxylated polyether), as well as tests by others on melamine-based superplasticizers, it is concluded that superplasticizers used in concrete in emplacement drifts will probably not be decomposed to release CO₂ under temperatures up to 200°C. Also, due to the absence of carbon dioxide, carbonation of the concrete due to this evolution process is not expected to occur under this situation. As a result, the pH value of cement paste solution will not be lowered due to the existence of organic superplasticizers in concrete. However, it should be noted that carbonation caused by air in the drifts may occur, but this was not a subject of this study.

Although the time period for the gas evolution tests is very short compared with the long operation life of the repository, the above conclusion is expected to remain valid because the addition of superplasticizers in cement does not affect the fundamental structure of hydration. Besides, the function of superplasticizers only occurs within the first few hours after concrete is mixed. Nevertheless, it seemed to be necessary to conduct some gas evolution tests for longer periods, say three months to half a year or longer, due to the low degradation rate of the superplasticizer in the testing condition. If the results from these longer periods still do not change, it will probably be evident enough to confirm the above conclusion.

The pH values of the expressed pore fluids for the different formulations at different ages were measured. All pH values are generally lower than those of normal cement pastes without silica fume which are controlled by the alkali from the cement at a value of approximately 13.5. These values indicate a greater extent of incorporation of alkalis by the additional C-S-H phases formed by the reactions of silica fume with calcium-bearing phases and more nearly approach the values established by Ca(OH)₂ of 12.4. However, it should be noted that these are pH values determined for normal temperature curing, and do not reflect the lower pH values characteristic of high temperature curing of silica-rich compositions. Since the temperature at emplacement drifts will be higher than 85 °C for a prolonged period (up to thousands of years), the crystallation of C-S-H gel will probably be complete and reduce the pH to a lower value. Especially for the high-silica concrete mix design, the silica fume content is greater than 30% of cementitious material and the cement content is low, therefore, the eventual pH value of concrete

cement paste solution may be lowered below 10 during the postclosure period.

The amounts of high-range water reducers (or superplasticizers) for the two proposed concrete mix design options were presented. It should be noted that those amounts are preliminary. The actual dosage will not be known until the final mix design has been approved and trial mixes have been conducted. Although the superplasticizers in concrete will increase the total organic materials in the repository, the significance of this increase can only be judged when realistic assessment of the quantity and type of organic materials from other sources, which include naturally occurred and introduced (or man-made), in the repository are available. An adequate knowledge of quantity and location of organic materials from these sources is necessary for evaluation of long-term postclosure performance.

The results of investigation of biodegradation of naphthalene-based superplasticizer by bacteria provide a good insight regarding the potential use of superplasticizers by bacteria. The preliminary conclusion is that superplasticizers (especially long-chain) will probably not be used as nutrients for bacteria in repository conditions as long as a hot ($>120^{\circ}\text{C}$) and dry condition for an extended period is maintained. However, since the testing was performed in a low temperature environment for a short period and only for one specific superplasticizer, it seems desirable to perform similar tests using cement paste samples containing various superplasticizers (different chemical types) subjecting to low and high temperatures ($>120^{\circ}\text{C}$) for longer periods, e.g., three months or longer to confirm this conclusion.

In summary, the results of this analysis have provided very useful information regarding the chemical evolution of organic admixtures in concrete under dry and elevated temperatures, alkalinity in cementitious repository, and the biodegradation of superplasticizers at ambient temperatures. However, based on the foregoing discussions, additional testings and investigations are recommended as follows:

- Conduct gas evolution tests for cement paste samples containing a range of superplasticizers, such as Rheobuild 1000 and 3000, and others for longer periods, say three to six months or longer. Measure, if possible, the kinetics (reaction rate) of the degradation of the cement paste samples containing superplasticizers.
- Conduct above tests with Type V cement because Type V cement is proposed for repository use and the results of testing may be different from that made with Type II cement due to different physico-chemical properties.
- Perform tests on biodegradation of superplasticizers and concrete or cement pastes containing superplasticizers at dry and elevated temperatures that are expected at repository emplacement drift environment.
- Assess the types and quantities of organic materials from other sources in the repository.

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9. ATTACHMENT

**Final Report of Laboratory Testing of Evolution of Organic Admixtures in Concrete, prepared by
Materials Research Laboratory, The Pennsylvania State University.**

"Laboratory Testing of Evolution of Organic Admixtures in Concrete"

prepared for

TRW Environmental Safety Systems, Inc

by

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EXECUTIVE SUMMARY

This study was initiated to evaluate the reactivity of the organic components of cementitious materials which had been formulated with organic-based superplasticizers. By utilizing mass spectroscopy and examining the gases released during the thermal processing of the paste samples, the presence of CO_2 could be correlated with the thermal decomposition of the organic superplasticizer.

The gas evolution studies on the Rheobuild superplasticizer containing pastes in which carbon dioxide was specifically monitored at temperatures up to 300°C were negative for carbon dioxide. Two possible scenarios could account for the observations in these studies. The superplasticizer would be stable at the temperatures of the study or the superplasticizer would decompose and result in the production of predominantly carbon dioxide and water. In the latter case, it is possible that the decomposition products would react with the calcium hydroxide or dehydrated calcium silicates to form calcium carbonate and not be observed in the off gas atmosphere.

In order to differentiate between the two possible scenarios that described observations, the thermal stability of the dehydrated superplasticizer was examined and it revealed that under the conditions of the experiment, it too did not release any carbon dioxide. Based on these observations, it is speculated that the superplasticizer reported dispersed onto the cement paste system is stable within the time and temperature interval of the study.

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INTRODUCTION

Currently, the Repository Design is considering concrete linings (either precast or cast-in-place) as an option for ground support in the emplacement drifts. These linings will provide for the stability of the emplacement drifts throughout the pre-closure period, and will be left in place at closure. However, the potential long-term evolution of cementitious materials in the repository drift environment during the post-closure period, may have some adverse geochemical effects due to potential generation of high pH pore solutions in concrete when the concrete is fabricated with ordinary Portland cement.

In order to mitigate the potential problems associated with high pH solutions (could reach 13.5) with ordinary Portland cement, the concrete can be engineered by adding pozzolans such as silica fume to reduce the pH values. Based on the Performance Assessment (PA) Group's recommendation, a pH of about 10 or lower is desirable to ensure the long-term geochemical stability of the repository system. In view of this recommendation, in cement-silica fume systems, a superplasticizer (an organic admixture) is normally added for deflocculating the paste. However, the use of the organic admixtures will introduce additional organic materials to the repository environment and may cause other post-closure performance problems. The organic materials introduced could provide nutrients for the growth of microbial activity, which could introduce additional organic acids and colloids which would enhance waste form degradation and radionuclide mobility. All these phenomena could lead to enhanced transport of radionuclides in the potential repository.

STATEMENT OF PROBLEM

The current limit for the amount of post-closure organics is "as close to zero as practical." Because the organic admixtures added to the concrete mix would probably be the major source of organics introduced to the potential repository, estimation of the organic contents that will remain is important in assessing the potential post-closure performance problems discussed above.

It is expected that the post-closure emplacement drifts will be very dry at temperatures above 100°C for an extended period of time. It is postulated that under this dry and elevated temperature environment, the organic admixtures in the concrete will be decomposed and volatilized as gases, mostly CO₂ with other minor components such as SO₂ and NO_x. The common backbones of most organic admixtures may be disintegrated into forms with shorter carbon chains (lower molecular weights) and strongly adsorbed on the hydrated phases. Portions of the CO₂ gas evolved are likely to escape into the emplacement drift and repository rock. Remaining portions of the CO₂ gas evolved could react with the cement hydrated phases [such as portlandite Ca(OH)₂, calcium silicate hydrate (C-S-H) phases, and other hydrated phases].

This reaction would result in the formation of calcium-carbonate minerals (mostly calcite CaCO_3). This process is called carbonation and consumes the hydrated cement phases, especially portlandite which is responsible for generating the pore solution at pH of 12 to 12.5. Thus, the carbonation process lowers the pore solution pH. Most importantly, as a result of this evolution of the organic admixtures, the remaining organic materials in the concrete may be reduced substantially, which may be acceptable to PA's requirement for long-term post-closure performance of the repository.

This research team has postulated that if the superplasticizer in these formulations did decompose, that it would convert to carbon dioxide and water. Furthermore, the presence of calcium hydroxide and hydrous calcium silicate gel in the cementitious components of the pastes could react with the carbon dioxide to further retain it in the solids.

BACKGROUND

Role of Superplasticizers and Their Evolution During Cement Paste Processing, Hardening and Aging.

The major role of organic superplasticizing admixtures is to achieve water-reduction and promote increased fluidity or workability in cement paste and concrete mixtures. Superplasticizers are an essential component of silica fume-containing concretes, in particular, because of the very high surface area of the silica fume, which substantially increases the water requirement of the concrete. It is widely agreed that water reduction is effected through improved dispersion of the cement grains in the mixing water where flocculation is decreased or prevented and the water otherwise immobilized within the flocs is added to that in which the particles can move. At least three principal types of superplasticizers are in common use: salts of 1) sulfonated naphthalene formaldehyde condensate polymer (e.g. Rheobild), 2) poly (melamine sulfonate) and 3) modified lignosulfonate materials. A number of newer types of superplasticizers including carboxylated polyethers (e.g. ADVA) appear to have significantly different functions in the slurries and may be used in smaller proportions to increase fluidity, but are not yet widely used in practice.

The most widely studied effects of organic superplasticizers are those early effects taking place in the paste suspension. Adsorption of the admixture on the hydrating cement grains could decrease flocculation in at least three ways. The first is an increase in the magnitude of the zeta-potential (surface potential); if all the particles carry a surface charge of the same sign and sufficient magnitude, they will repel each other. The second is an increase in solid-liquid affinity; if the particles are more strongly attracted to the liquid than to each other, they will tend to disperse. The third is steric hindrance; the oriented adsorption of a complex (usually non-ionic) polymer can weaken the attraction between solid particles. It has been well established that the major

superplasticizing effect in naphthalene-based materials is that of electrostatic repulsion and the magnitude of the effect generally increases with increasing molecular weight of the polymer. Some carboxylated polyethers, in contrast, are less adsorbed by the cement particles and appear to achieve their superplasticizing effect dominantly by steric hindrance rather than simple electrostatic repulsion.

Superplasticizers have been shown to increase the fluidity of C_3S pastes much as they do that of cement pastes. However, there is variation with cement compositions. Studies on individual anhydrous and hydrated compounds in aqueous and non-aqueous media indicate that calcium lignosulfonate and superplasticizers are adsorbed by C-S-H, AFm phases or CH. Simple lignosulfonates or other organic species have been shown to enter the interlayer sites of AFm (hydrated calcium aluminate or calcium monosulfaluminate) where they may presumably become fixed in the crystal structure. It has also been suggested that such organic species may become intercalated as interlayers in the C-S-H structure; where they also, presumably may be "fixed" as the cement paste hardens.

Considerable information is available on the changes taking place in the early-age in the composition of cement pastes suspensions containing superplasticizers, during the first few minutes to an hour or two, where the relative proportions of organic species "sorbed" on cement particles are contrasted with that portion remaining in solution. These phenomena have been investigated in order to better understand the mechanisms of their action as superplasticizers. However, there has been relative little interest in determining the evolutionary changes of the superplasticizers with time, and their role in the final hardened structure. Difficulties have been encountered in carrying out such studies, in particular, contrasting the nature of the superplasticizers affixed to the solid C-S-H or calcium aluminate hydrate vs. that remaining in pore solution. Such studies are, of course, made more difficult by the fact that the major role of the superplasticizers is to decrease the W/C; thereby, relatively little "pore solution" remains available for extraction and examination in mature hardened pastes. Some relatively few studies have been performed on mature hardened pastes in attempt to extract organic admixtures using organic solvents, without much success, suggesting that the admixtures become firmly bound in the hardened paste structure.

The thermal stability of the sodium salt of sulfonated naphthalene formaldehyde condensate polymer is contrasted to the stability of the other commonly used superplasticizers in the only other literature citation on this subject by Feylessoufi et al., (1997). In this study, they reported, that they anticipated evolution of "...volatile decomposition products of the superplasticizer and carbon dioxide..." from the thermal treatment of reactive powder concretes containing poly (melamine sulfonate). Their findings, though not directly applicable to naphthalene-based superplasticizers, suggest

that the decomposition of the superplasticizer [type identified as a polymelamine] did not begin until temperatures exceeded 300°C and continued over a wide temperature range.

OBJECTIVE

The purpose of this study was to evaluate the thermal stability of the organic components of cementitious materials which had been formulated with organic-based superplasticizers. By utilizing mass spectroscopy and examining the gases released during the thermal processing of the paste samples, the presence of CO₂ could be correlated with the thermal decomposition of the organic superplasticizer.

MATERIALS FORMULATIONS

The studies were performed largely with Rheobuild 1000, a naphthalene-based superplasticizer, with a long-term history of use in the construction industry. In addition, a limited study was made of ADVA, a new proprietary carboxylated polyether superplasticizer, which can be used in smaller quantities than the naphthalene-based admixture.

Paste specimens were formulated so that they reflected the general proportions of Type II Portland cement, silica fume, water and superplasticizer identified as representative of potential concrete formulations but of course without the coarse and fine aggregates. Table I summarizes these formulations based upon the designated superplasticizer Rheobuild 1000. These variations reflect differences in the silica fume to cement ratios. All formulations were developed with approximately 4% by weight of as received liquid superplasticizer to cementitious components. This concentration reflects dosages at the maximum level and was selected to allow for the best possible identification of decomposition products of the organic portion if they were evolved.

CURING CONDITIONS

The curing conditions were selected to represent realistic conditions that the concrete might be anticipated to be exposed to during initial curing and the period prior to waste emplacement. To replicate these conditions, paste samples were cured in containers at near saturated relative humidity at 38°C for the initial 14 days after mixing. Curing was continued at 38°C and 30% RH over a solution of magnesium sulfate which controlled the relative humidity at 30% for an additional 14 days.

Table I
Formulations Tested [weight %]

	TRW-1	TRW-2	TRW-3*	TRW-5**
Type II Cement	68.70	56.00	53.44	66.16
Silica Fume	7.60	24.00	22.90	7.32
Water	20.60	16.80	20.61	23.52
Rheobuild 1000	3.10	3.20	3.05	3.00
water/cementitious solids	0.27	0.21	0.27	0.32
silica fume/cementitious materials	0.10	0.30	0.30	0.10
superplasticizer/cementitious materials	0.041	0.04	0.04	0.041

* This mixture is similar to mixture TRW-2 except that the water content is higher and equals that of Mixture TRW-1 [water/(cement+silica fume) = 0.27].

** This mixture is similar to mixture TRW-1 except that the water content is higher [water/(cement+silica fume) = 0.32].

APPARATUS

The mass spectroscopy technique was used to measure the partial pressure of the gases resulting as potential degradation products of the superplasticizer components in different samples of pastes after 28 days of curing. An Ametek quadrupole mass spectrometer model M100M was used (Figures 1-3) to investigate blanks, reference samples and pastes. A schematic of the conventional glassware gas evolution apparatus is shown in Figure 4. The apparatus consists of conventional 24/40 pyrex ground glass fitting connectors. The apparatus was designed with a test tube to hold the paste samples inside of a Kanthal wound resistance furnace custom made for this apparatus and designed to operate at 300°C, the maximum temperature of this study. The furnace was controlled with an Omega, model CN4800, ramp temperature controller which had its controlling thermocouple placed on the outside of the test tube reactor between it and the furnace heating elements. The apparatus was fitted with an inlet for temperature monitoring using a type K thermocouple which was placed near the crushed paste and the fused quartz capillary tube which sampled the test tube atmosphere and conducted the gases into the quadrupole mass spectrometer. This inlet was also adapted to conduct gases directly onto the crushed paste. The top section of the sample tube is shown in Figure 4 where the thermocouples and the quartz capillary sample tube (connected to the mass spectrometer) are shown. As originally designed, the exiting gases were expelled by the use of a vacuum pump. As a

recommendation to the design of the apparatus, the pump system was replaced by a net positive internal pressure delivered by a gas cylinder for the final set of tests. The entering gas stream could be conditioned with an optional ascarite CO₂ trap, an optional zeolite water trap and a liquid nitrogen cold trap.

EXPERIMENTAL AND TEST PLAN

Compressive strengths of the specimens at 1, 3, 7, 14 and 28 days were determined following ASTM C 109 protocol (C 109 protocol calls for mortar cubes to be 2 inches on an edge, specifies loading rate, testing intervals and calculational procedures). The samples from the compressive strength testing were then freeze dried for use in the study of the reactivity of the superplasticizer. Because of concerns that freeze-drying could impact the behavior of the paste, the procedure of drying was modified with sample TRW-5. Samples at 1 and 3 days were freeze-dried as normal; then the drying methodology was modified and remaining samples of TRW-5 at 7, 14 and 28 days were D-dried. This method of drying involves vacuum desiccation of crushed samples at room temperature, trapping the water in a liquid nitrogen trap located just upstream of the vacuum pump. The majority of the free-water is removed within the first few hours of treatment but the recommended approach is to hold the sample under these conditions for four days. Unlike the freeze-drying method where hydration and carbonation are arrested by freezing, the D-drying method requires two precautions:

- 1) The sample must be crushed in a CO₂-free atmosphere to avoid carbonation and,
- 2) The grains are much finer than in the freeze-drying method in order to ensure faster evaporation of water and avoid further hydration of the sample. A maximum grain size of 600µm is used in the D-drying procedure by screening and collecting the specimens that pass through a #30 sieve (Copeland et al., 1953).

Characterization of all samples was by x-ray diffraction and scanning electron microscopy at all ages.

Pore solution extraction and pH measurements on the extracted fluids were made at all ages. The apparatus depicted in Figure 5 was utilized. It employed a uniaxial plunger and die in a hydraulic press equipped with a collection drain connected to a laboratory syringe. The expressed liquid was not exposed to atmospheric conditions during the operation. All liquid samples recovered in this manner were filtered and the pH immediately determined by a pH meter referenced to buffer solutions at pH 3, 5 and 10. The pH electrode used for these measurements is a commercially available glass electrode. The operation of this device depends upon the difference in potential across a glass membrane separating solutions in two half cells; one containing a platinum electrode and the other a calomel reference electrode.

RESULTS

1) Compressive Strength:

The compressive strength values (MPa) of the different formulations at different ages are shown in Table II and presented graphically in Figures 7-10. Figure 11 shows a typical failure mode for cement pastes tested in this study. These data indicate mean gains in strength ranging from 20 to 102% at 28 days.

2) pH of Pore Solution:

The pH values of the expressed pore fluids for the different formulations at different ages are shown in Table III. They are generally lower than those of normal cement pastes without silica fume which are controlled by the alkali from the cement at a value of approximately 13.5. These values indicate a greater extent of consumption of alkalis by silica fume and more nearly approach the values established by $\text{Ca}(\text{OH})_2$ of 12.4. However, it should be noted that these are pH values determined for normal temperature curing, and do not reflect the lower pH values characteristic of high temperature curing of silica-rich compositions (Scheetz et al., 1989).

3) X-ray Diffraction:

The x-ray diffraction patterns at different ages are shown in Figures 12-17 for formulations TRW-1 and Figures 18-23 for formulation TRW-3. Figures 17 and 23 summarize sets of x-ray patterns at all ages for TRW-1 and TRW-3, respectively.

Table II
Compressive Strength (MPa) at Different Ages and Formulations*

	TRW-1	TRW-2	TRW-3	TRW-5
1 Day	43.56 ± 5.34	48.15 ± 4.26	59.30 ± 0.88	25.28 ± 1.97
3 Days	59.39 ± 4.87	57.15 ± 5.99	59.70 ± 1.13	37.76 ± 10.25
7 Days	61.66 ± 6.20	59.63 ± 6.41	59.67 ± 1.13	40.95 ± 1.22
14 Days	63.05 ± 1.36	62.04 ± 10.39	61.62 ± 1.39	47.32 ± 1.89
28 Days	73.91 ± 3.44	61.32 ± 6.61	70.97 ± 2.79	51.16 ± 0.76

* Average of 3 samples.

Table III
pH Values at Different Ages

	TRW-1	TRW-2	TRW-3	TRW-5
1 Day	n/a	n/a	12.70	12.60
3 Days	n/a	n/a	12.60	12.67
7 Days	12.60	n/a	12.60	12.72
14 Days	12.90	n/a	12.60	12.70
28 Days	n/a	n/a	n/a	n/a

n/a - Could not obtain pore solutions.

TRW-1 contains portlandite up to 28 days, while sample TRW-3 no longer contains portlandite at 7 days and beyond, reflecting the higher silica fume content. The C-S-H (major hydration product of cement) appears to be in a gel form. It appears that the hydration reaction is not yet completed at 28 days of age as shown by the presence of the residual alite.

4) Electron Microscopy

Scanning electron micrographs of the samples TRW-1 and TRW-3 at different ages are shown (at two different magnifications) in Figures 24 through 43. A low porosity dense microstructure is evident in all micrographs. In addition, crystals of portlandite, usually observed in normal portland cement pastes without silica fume are not found in the micrographs. The dense microstructure is the result of the combined effects of silica fume and the low water to cement ratio. This microstructure is different from that of normal cement pastes at the same ages and with comparable water to cement ratio. In the latter, a more porous microstructure and the presence of crystals of $\text{Ca}(\text{OH})_2$ is very apparent (Malhotra, 1987). In pastes containing silica fume, however, they appear to be more consolidated and exhibit a vitreous-like appearance. This vitreous-like appearance may be due to the existence of a higher proportion of a gel form of C-S-H. Due to the presence of excess silica in the pore solutions of pastes containing silica fume, low calcium to silica (C/S) ratio C-S-H is formed. This is probably the origin of the vitreous-like appearance of the microstructure. Some investigators have determined the C/S ratio of C-S-H of pastes containing silica fume of 0.9/1 to 1.3/1 (Traettberg, A., 1978; Regourd et al., 1982; Regourd et al., 1983) compared to 1.7/1 in normal cement pastes without silica fume.

5) Mass Spectroscopy

5. a) Mass Spectroscopy of the Superplasticizers

5.a.1) Master Builders Rheobuild 1000

A sample of Rheobuild 1000 was initially dried in an oven at 100°C for 24 hours to remove free water and the resulting solid phase was subjected to the vapor evolution experiment in the Quadrupole mass spectrometer. The results are shown in Figure 44. The results show evolution of water only. The absence of carbon dioxide and oxygen may be interpreted as indicative of the thermal stability of the superplasticizer under the experimental conditions.

5.a.2) WR GRACE ADVA Concrete Additive

Upon drying in an oven at 100°C over night, the fluid lost ~65% of its mass, corresponding to its water content. The residue was a thick, light brown liquid. The residue was collected and evaluated by mass spectroscopy.

Upon application of vacuum in the mass spectrometer apparatus, the fluid boiled violently. Results (Figure 45) show the expulsion of water vapor, nitrogen and carbon dioxide. Upon termination of the experiment, a considerable loss in the quantity of fluid was detected. The expulsion of carbon dioxide and nitrogen may be an indication of the thermal instability of this compound under the experimental conditions. It also served to re-confirm that the monitor was sensitive to carbon dioxide. Beyond the above, no detailed experiments were planned or performed with the addition of ADVA to cementitious materials, as this was considered beyond the scope of the present study. Such experiments would be useful to test the ability of the cementitious materials to "fix" the carbon dioxide released at higher temperatures.

5. b) Mass Spectroscopy of the Cement Samples

5.b.1) TRW-1, TRW-2, and TRW-3

Results of mass spectroscopy tests on crushed portions of freeze-dried samples of the formulations TRW-1, TRW-2, and TRW-3 at 28 days age show the expulsion of some water vapor (Figures 46-48 for TRW-1, TRW-2, and TRW-3 respectively). Again the absence of carbon dioxide and oxygen may be an indication of the lack of reactivity of the superplasticizer under the experimental conditions or else its thermal stability.

5.b.2) TRW-5

The mass spectroscopy experiments on sample TRW-5 cured for 28 days were carried out after two modifications were done. First, the sample was D-dried instead of using freeze-drying. Second, the quadrupole mass spectroscopy experiment was modified to allow for a continuous flow of carbon dioxide-free air through the cement sample throughout the entire test. A blank experiment was carried out with air flowing without sample. Results of the D-dried sample at 28 days age show the carbon dioxide water evolution for a mixed gas containing ~80% nitrogen and ~20% oxygen, Figure 49. A comparable run was conducted utilizing "medical" air which is nothing more than dry compressed air, resulting in the measurement shown in Figure 50. Figure 51 is a photograph of a typical sample of D-dried cement paste after testing. Contrasting these two data sets shows that the commercially prepared mixed gases simulated air contained appreciable amounts of water. By contrast the "medical" air indeed was essentially water free. However, neither experimental run indicated the presence of carbon dioxide, above detection limit.

DISCUSSION

During the course of this study, recommendations were made with regard to the experimental design that was implemented. The initial design of the apparatus had the paste sample heated under a vacuum. This condition, it was felt, could cause the decomposition of the organic superplasticizer in the presence of a reduced oxygen fugacity and as such may result in charring of the superplasticizer rather than a decomposition into carbon dioxide. To address these concerns, the system was modified so that both a mixture of gases [nitrogen and oxygen only] or dry, medical air with an ascarite carbon dioxide scrubber were introduced into the reaction zone at test temperatures. The pressure of the inflowing gas mixtures instead of the vacuum pump flushed the gases from the system and past the mass spectrometer intake.

The results of all of the gas evolution studies on the Rheobuild superplasticizer in which carbon dioxide was specifically monitored were negative for carbon dioxide. Based on our initial thesis that if the superplasticizer would decompose at 300°C, 100°C above design maximum limit that the concrete liner of the waste tunnel would see, it would result in the production of predominantly carbon dioxide and water. Furthermore, it was postulated that it is very likely that the decomposition products would react with the calcium hydroxide or dehydrated calcium silicates to form calcium carbonate and not be observed in the off gas atmosphere.

The failure to observe any carbon dioxide in the off gas emissions of any of these tests does not support the initial thesis of this study. Furthermore, the study of the thermal reactivity of Rheobuild 1000 by itself suggests that it is

thermally stable within the time/temperature/transformation interval that was studied, as indicated by Figure 44.

CONCLUSIONS

Two possible scenarios could account for the observations in these studies. 1) The superplasticizer is stable at the temperatures of the study. 2) The superplasticizer would decompose and result in the production of predominantly carbon dioxide and water which would react with the calcium hydroxide or dehydrated calcium silicates to form calcium carbonate and not be observed in the off gas atmosphere.

The gas evolution studies on the Rheobuild superplasticizer containing pastes in which carbon dioxide was specifically monitored at temperatures up to 300°C were negative for carbon dioxide. In order to differentiate between the two possible scenarios that described observations, the thermal stability of the dehydrated superplasticizer was examined and it revealed that under the conditions of the experiment, it too did not release any carbon dioxide. Based on these observations, it is concluded that the superplasticizer dispersed onto the cement paste system also did not release carbon dioxide under the experimental conditions.

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Fig. 1: Ametek quadrupole mass spectrometer model M100M. A general view.

Fig. 2: Ametek quadrupole mass spectrometer model M100M.
A side view showing the electronic module.

Fig. 3: Ametek quadrupole mass spectrometer model M100M.
A side view showing the turbo pump and the filament.

Fig. 4: Top Section of the sample tube where the thermocouples and the quartz capillary sample tube (connected to the mass spectrometer) are shown.

Fig. 5 : Schematic of the gas evolution apparatus.

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Fig. 6: Schematic of the pore fluids extrusion apparatus. Cement cylinders are compressed in piston-cylinder die to free pore fluids, which are collected via syringe.

Fig. 7: Compressive strength versus age of TRW-1.

Fig. 8: Compressive strength versus age of TRW-2.

Fig. 9: Compressive strength versus age of TRW-3.

Fig. 10: Compressive strength versus age of TRW-5.

Fig. 11: Typical failure mode for cement paste samples tested in this study.

Fig. 12. X-ray diffraction pattern of the sample TRW-1 at 1 day.

Fig. 13. X-ray diffraction pattern of the sample TRW-1 at 3 day.

Fig. 14. X-ray diffraction pattern of the sample TRW-1 at 7 day.

Fig. 15. X-ray diffraction pattern of the sample TRW-1 at 14 day.

Fig. 16. X-ray diffraction pattern of the sample TRW-1 at 28 day.

Fig. 17. Composite X-ray diffraction pattern of the sample TRW-1.

Fig. 18. X-ray diffraction pattern of the sample TRW-3 at 1 day.

Fig. 19. X-ray diffraction pattern of the sample TRW-3 at 3 day.

Fig. 20. X-ray diffraction pattern of the sample TRW-3 at 7 day.

Fig. 21. X-ray diffraction pattern of the sample TRW-3 at 14 day.

Fig. 22. X-ray diffraction pattern of the sample TRW-3 at 28 day.

Fig. 23. Composite X-ray diffraction pattern of the sample TRW-3.

Fig. 24: Low magnification scanning electron micrograph of the sample TRW-1 after curing for 1 day.

Fig. 25: High magnification scanning electron micrograph of the sample TRW-1 after curing for 1 day.

Fig. 26: Low magnification scanning electron micrograph of the sample TRW-1 after curing for 3 days.

Fig. 27: High magnification scanning electron micrograph of the sample TRW-1 after curing for 3 days.

Fig. 28: Low magnification scanning electron micrograph of the sample TRW-1 after curing for 7 days.

Fig. 29: High magnification scanning electron micrograph of the sample TRW-1 after curing for 7 days.

Fig. 30: Low magnification scanning electron micrograph of the sample TRW-1 after curing for 14 days.

Fig. 31: High magnification scanning electron micrograph of the sample TRW-1 after curing for 14 days.

Fig. 32: Low magnification scanning electron micrograph of the sample TRW-1 after curing for 28 days.

Fig. 33: High magnification scanning electron micrograph of the sample TRW-1 after curing for 28 days.

Fig. 34: Low magnification scanning electron micrograph of the sample TRW-3 after curing for 1 day.

Fig. 35: High magnification scanning electron micrograph of the sample TRW-3 after curing for 1 day.

Fig. 36: Low magnification scanning electron micrograph of the sample TRW-3 after curing for 3 days.

Fig. 37: High magnification scanning electron micrograph of the sample TRW-3 after curing for 3 days.

Fig. 38: Low magnification scanning electron micrograph of the sample TRW-3 after curing for 7 days.

Fig. 39: High magnification scanning electron micrograph of the sample TRW-3 after curing for 7 days.

Fig. 40: Low magnification scanning electron micrograph of the sample TRW-3 after curing for 14 days.

Fig. 41: High magnification scanning electron micrograph of the sample TRW-3 after curing for 14 days.

Fig. 42: Low magnification scanning electron micrograph of the sample TRW-3 after curing for 28 days.

Fig. 43: High magnification scanning electron micrograph of the sample TRW-3 after curing for 28 days.

Fig. 44: Results of mass spectroscopy of Rheobuild 1000.

Fig. 45: Results of mass spectroscopy of ADVA concrete additive.

Fig. 46: Results of mass spectroscopy of a freeze-dried sample of TRW-1 after curing for 28 days.

Fig. 47: Results of mass spectroscopy of a freeze-dried sample of TRW-2 after curing for 28 days.

Fig. 48: Results of mass spectroscopy of a freeze-dried sample of TRW-3 after curing for 28 days.

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Fig. 49: Results of mass spectroscopy of a D-dried sample of TRW-5 after curing for 28 days. The test was conducted with a mixture of ~20% oxygen and 80% nitrogen flowing through the sample.

Fig. 50: Results of mass spectroscopy of a D-dried sample of TRW-5 after curing for 28 days. The test was conducted with "medical" air flowing through the sample.

Fig. 51: A photograph of a typical sample of D-dried cement paste after testing.