

EVALUATION OF CEMENT STABILITY

K. Chino and H. Yusa
Energy Research Laboratory, Hitachi, Ltd.
Hitachi, Japan 316

ABSTRACT

Cement stability is theoretically evaluated to provide stable cement packages and storage methods without deterioration. A computer code was developed to calculate equilibrium composition based on minimization of Gibbs free energy of the system considered. It is found that increase of storage temperature and addition of NaOH are two effectual methods to avoid sulphate attack.

INTRODUCTION

Long-term stability of waste packages is required to protect the general population from releases of radioactivity. As such, cement-based material is widely used to solidify radioactive wastes and manufacture containers. It is the purpose of this paper to evaluate the cement stability to provide stable cement packages and storage methods without deterioration.

Empirical equations,¹ based on a few factors, have been proposed to estimate the cement stability. But their application must be limited to within the experimental region because there are many other factors which affect stability. Since cement deteriorates at a very slow rate, it is difficult to collect sufficient data.

Therefore, the authors tried to theoretically evaluate cement stability. The cement chemical system is so complex that a detailed reaction mechanism has not been clearly stated. It is difficult to simulate its hydrating processes. A computer program was developed to compute the equilibrium composition of the solidified cement. The equilibrium calculation was based on a method to minimize the Gibbs free energy of the system considered. Pore volume ratio which greatly affects the stability could be computed from the equilibrium composition. The program was modified to simulate hydrating processes. And storage conditions to avoid sulphate attack were evaluated.

CALCULATIONS

Table I shows the 56 compounds considered which are combinations of CaO, SiO₂, Al₂O₃, H₂O, Na₂O, and SO₃. The first three stable oxides are the main components of cement and the last two are typical impurities in ground water. The compounds in Table I are listed by the shortened notation commonly used by cement chemists, where each oxide is described by one letter such as C=CaO. Gibbs free energy data from 25°C to 227°C are stored in the program to evaluate temperature effect on the equilibrium composition.²⁻⁸ Density data are also stored to compute the pore volume ratio.⁹⁻¹¹

Two methods have been proposed for computing thermodynamic equilibrium compositions by Brinkley and White. Brinkley's method computes the equilibrium composition using equilibrium constants of chemical reactions. But this method cannot be used when the reaction processes are not known. In the complex cement chemical system, it is necessary to use White's method which selects compounds to minimize the total

Gibbs free energy. The total Gibbs free energy of the cement system can be expressed as:

$$G_T = \sum_i n_i (G_{li} + R T \ln(n_i / \sum_i n_i)) + \sum_i n_i G_{ci} \quad (1)$$

where

G_T = total Gibbs free energy (kJ/mol),

n_i = moles of compound i (mol),

G_i = Gibbs free energy of compound i (kJ/mol),

R = ideal gas law constant (kJ/(mol °K)),

T = absolute temperature (°K)

The subscripts l and c indicate solution and condensed phase, respectively. The constraints that the masses of all elements must be conserved are expressed by the subsidiary relationships:

TABLE I

Chemical Compounds in Cement Chemistry

System	Anhydrite	Hydrate
CaO-SiO ₂	C, S, C ₂ S, C ₃ S.	H, CH, SH, SH ₂ , S ₂ H, S ₂ H ₃ , CS ₂ H ₂ , C ₂ SH _{7/6} , C ₂ S ₃ H _{5/2} , C ₃ S ₂ H ₃ , C ₄ S ₃ H _{3/2} , C ₅ S ₆ H ₃ , C ₅ S ₆ H _{21/2} , C ₆ S ₆ H, C ₅ S ₆ H _{11/2}
Al ₂ O ₃ -SiO ₂	A, AS, AS ₂ , A ₃ S ₂	AH, AH ₃ , AS ₂ H ₂ , AS ₄ H
CaO-Al ₂ O ₃	CA, CA ₂ , C ₃ A, C ₁₂ A ₇	CAH ₁₀ , C ₂ AH ₈ , C ₃ AH ₆ , C ₄ AH ₁₃ , C ₄ AH ₉
Na ₂ O-SiO ₂	N, NS, NS ₂ , N ₂ S, N ₃ S, NA, NAS ₂ , NAS ₄ , NAS ₆	NH, NAS ₄ H ₂
Na ₂ O-SO ₃ -CaO- Al ₂ O ₃ -SiO ₂	NS, CS, AS ₃	NSH ₁₀ , N _{1/2} SH _{1/2} , CSH _{1/2} , CSH ₂ , C ₃ ACSH ₁₂ , C ₃ AC ₃ S ₃ H ₃₁

Abbreviation : C=CaO, S=SiO₂, H=H₂O, A=Al₂O₃, S=SO₃, N=Na₂O

$$\sum_i b_{ij} n_i = c_j \quad (2)$$

where

b_{ij} = coefficient on element j of compound i ,

c_j = moles of element j in the system (mol).

Because of the nonlinear term, $R T \ln(n_i / \sum_i n_i)$,

in Eq. (1), Lagrange's method of undetermined multipliers has usually been used to solve the above set of equations for gas and liquid equilibria. In the case of the cement system, however, no gas phase exists and the number of solutions can be assumed to be one. In the equilibrium state, the solution is saturated with condensed phases. Then, the nonlinear term in Eq. (1) can be computed by solubility data of compound i as shown in Eq. (3).

$$\begin{aligned} G_S &= G_{Ii} + R T \ln(n_i / \sum_i n_i) \\ &= G_{Ii} + R T \ln a_i \end{aligned} \quad (3)$$

where

G_S = Gibbs free energy of saturated solution (kJ/mol),

a_i = solubility of compound i .

After substituting the Gibbs free energy of saturated solution in place of the nonlinear term, Eq. (1) can be changed into a linear one as shown in Eq. (4).

$$G_T = \sum_i n_i G_{Si} + \sum_i n_i G_{Ci} \quad (4)$$

Solubility data of six saturated solutions are stored in the program to compute the Gibbs free energy of saturated solution.¹² The set of Eqs. (2) and (4) can be solved by a linear programming technique which can compute a more complex system than Lagrange's method of undetermined multipliers.

When the solidified cement contacts with ground water, impurities in water penetrate the cement through pores and deteriorating reactions takes place. Since it is important to reduce the pore volume ratio to maintain the stability, the pore volume of the solidified cement package is evaluated by Eq. (5):

$$a = \frac{(\sum_i n_i / \rho_i)_{\infty} - (\sum_i n_i / \rho_i)_{\infty} - (n_S / \rho_S)}{(\sum_i n_i / \rho_i)_{\infty}} \quad (5)$$

where

a = pore volume ratio,

ρ_i = density of compound i (kg/m³).

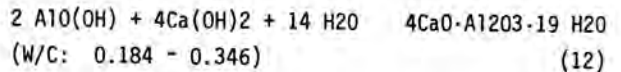
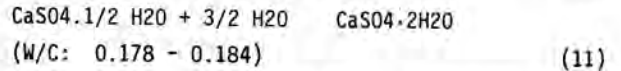
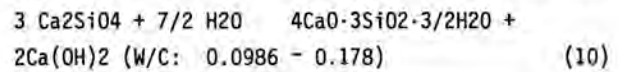
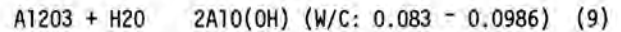
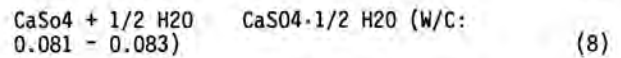
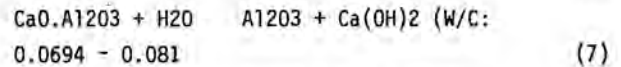
The subscripts \cdot and ∞ indicate initial and equilibrium states, respectively. The third term in Eq. (5) expresses the increase of the pore volume ratio obtained on evaporation of the saturated solution.

Table II shows parameters for computing the equilibrium composition. Portland cement type 1 was

selected because it is most widely used. Portland cement consists mainly of 3CaO·SiO₂, 2CaO·SiO₂, and 3CaO·Al₂O₃ which are stable at manufacturing temperature over 1600°C. Small amounts of calcium sulphate exist as an impurity in the initial composition. The effect of water to cement weight ratio on the pore volume ratio was computed in order to manufacture stable packages. And the effects of temperature and impurity were studied to avoid deterioration during long-term storage.

RESULTS AND DISCUSSION

The effect of the water to cement ratio (W/C) on the equilibrium composition is shown in Fig. 1 when Portland cement type 1 is cured at the standard temperature. As W/C is increased, the following seven hydration steps occur successively.



The change of total Gibbs free energy for one mole of H₂O hydration decreases as hydration proceeds; -58 kJ/mol for Eq. (6), -38.3 for Eq. (7), -16.4 for Eq. (8), -12.3 for Eq. (9), -11.0 for Eq. (10), -3.2 for Eq. (11), and 3.1 for Eq. (12). When W/C exceeds 0.35, all the water cannot be transformed into combined water and some Ca(OH)₂ saturated water remains in the solidified cement. Since Al₂O₃ transforms much free water into combined water, its initial content greatly affects the pore volume ratio.

TABLE II
Calculation Conditions

Parameter	Unit	Value
Composition	3CaO·SiO ₂	51.5
	2CaO·SiO ₂	26.3
	3CaO·Al ₂ O ₃	17.3
	CaSO ₄	3.1
	CaO	1.8
Temperature	°C	0 - 100
Water/Cement Ratio	—	0 - 0.5
Impurity	—	NaOH

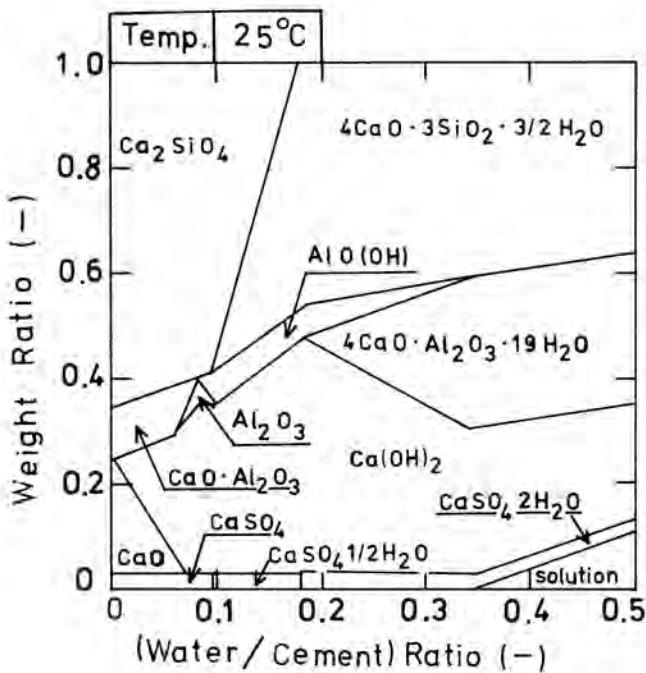


Fig. 1. Equilibrium composition of Portland Cement type 1.

Figure 2 shows the pore volume ratio which is computed from the equilibrium composition shown in Fig. 1. When free water is transformed into combined water, the total volume is reduced and micro pores are generated in the solidified cement. When the water to cement ratio exceeds 0.35, the pore volume ratio is greatly increased by evaporating the remaining solution. The measured volume ratio is 0.28 which is close to the computed result.¹³

Next, the computer program is modified to simulate hydrating processes. Figure 3 shows hydrating processes of Al₂O₃. The most stable aluminum compound is 4CaO·Al₂O₃·3CaSO₄·31H₂O and Al(OH)₃ is found to be the third. Hydrating processes in a complex chemical system can be estimated by this technique that eliminates stable compounds from the system considered.

Ettringite is well known for causing cracks in solidified cement because of its large molecular weight. It is experimentally observed that ettringite finally decomposes into more stable compounds. Hereafter the effect of storage conditions on ettringite production are evaluated to repress crack generation.

Figure 4 shows the effect of storage temperature on ettringite production. The equilibrium compositions without and with 4CaO·Al₂O₃·19H₂O are shown in Figs. 4 (a) and (b), respectively. Ettringite is generated as an intermediate product in Fig. 4 (a) when a cement package is stored under 44°C. Ettringite is decomposed as Eq. (13) if the storage temperature exceeds 44°C.



In the case of Fig. 4, 6.7 wt% ettringite is generated from CaSO₄ which exists in Portland cement

type 1. If SO₄ ion in ground water penetrates the solidified cement through pores and reacts with aluminum hydroxide and calcium hydroxide, the weight ratio of ettringite significantly increases to 68 wt%. The total volume may also increase 77%, causing many cracks in the solidified cement. The increase of storage temperature over 44°C provides one method to solve this problem.

When cement packages are stored at low temperature, the addition of strong base is an effective method to avoid generating cracks by ettringite. Figure 5 shows the equilibrium composition without 4CaO·Al₂O₃·19H₂O when NaOH is selected as a typical strong base to be mixed with Portland cement type 1.

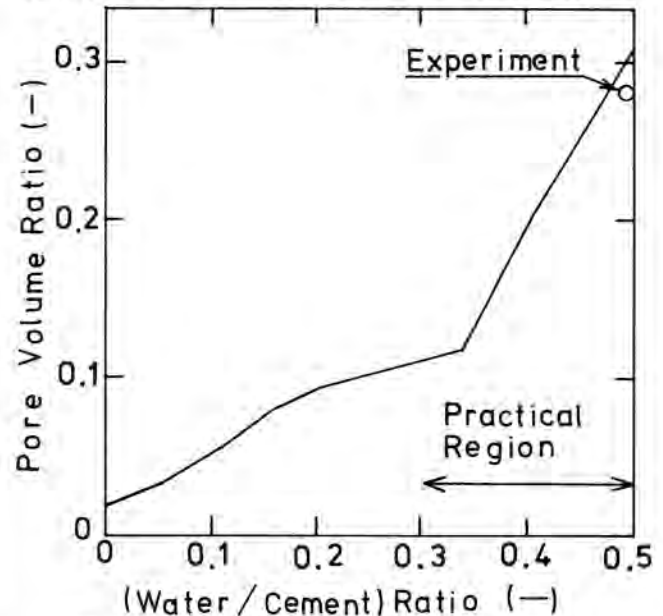


Fig. 2. Effect of water addition ratio on pore volume.

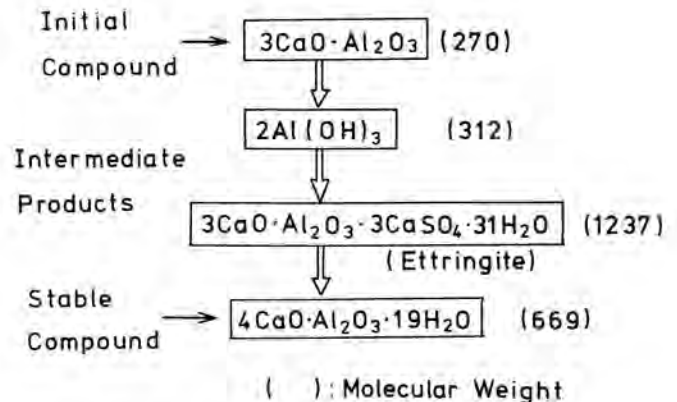


Fig. 3. Hydrating processes of aluminum oxide.

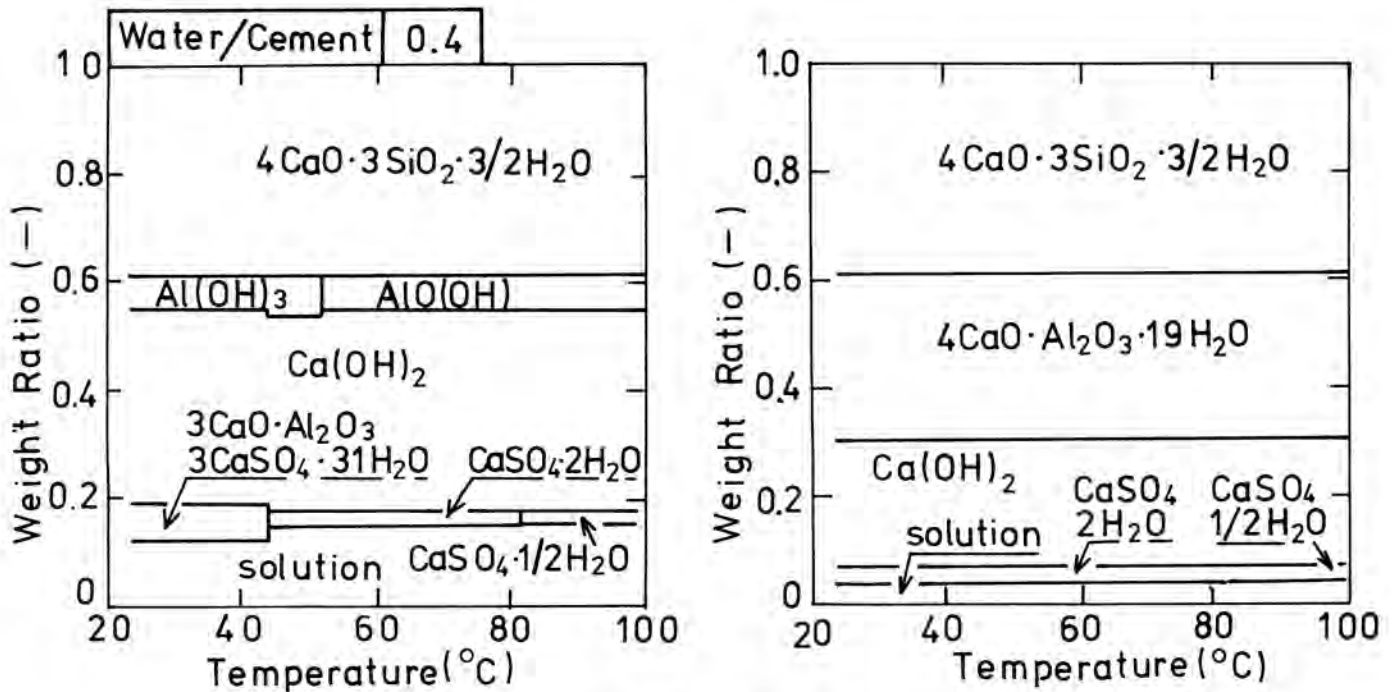
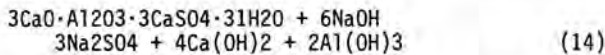
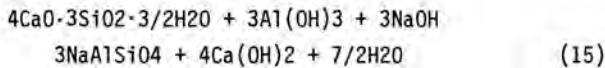


Fig. 4. Repression of ettringite production by increased storage temperature.

Since SO_4 is more stable as Na_2SO_4 than ettringite, the addition of NaOH



But if $(\text{NaOH}/\text{SO}_4)$ mole ratio exceeds 2, surplus NaOH reacts with $\text{Al}(\text{OH})_3$ and $4\text{CaO} \cdot 3\text{SiO}_2 \cdot 3/2\text{H}_2\text{O}$ as in Eq. (15).



Since NaAlSiO_4 is quite stable, it is advisable that the $(\text{NaOH}/\text{SO}_4)$ mole ratio be kept above 2.

CONCLUSION

The cement stability was theoretically studied to provide stable cement packages and store them without deterioration. The findings are summarized as follows:

1. A computer program was developed to calculate the equilibrium composition of the complex cement chemical system.
2. It was modified to estimate transient steps by eliminating stable chemical compounds.
3. Increase of storage temperature and addition of NaOH are two effective methods to avoid generating cracks by ettringite.

ACKNOWLEDGMENTS

This research was conducted at the University of Arizona. We wish to thank Dr. R. G. Post and Dr. J. G. McCray for many helpful suggestions during the course of this work.

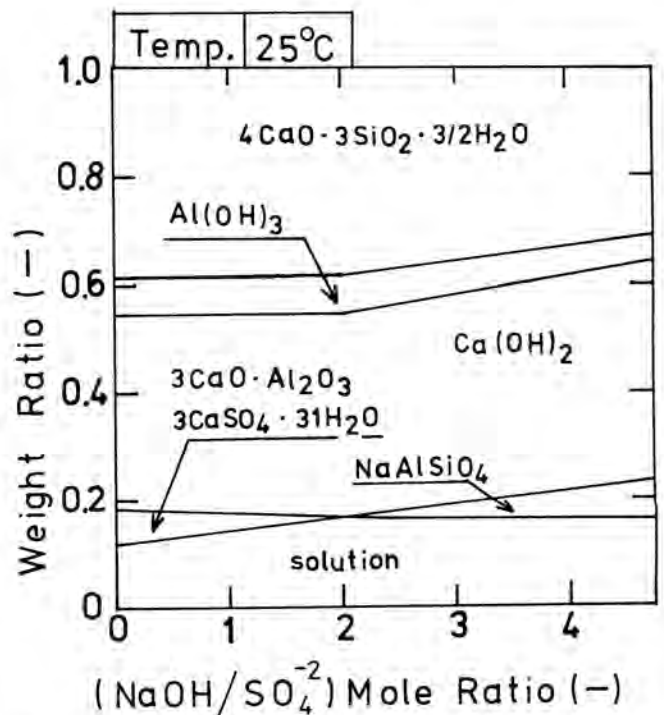


Fig. 5. Repression of ettringite production by addition of NaOH .

REFERENCES

1. C. D. Lawrence, "Durability of Concrete; Molecular Transport Processes and Test Methods," Technical report 544, Cement and Concrete Association.
2. S. R. Brinskley, Jr., "Note on the Conditions of Equilibrium for Systems for Many Constituents," *J. Chem. Phys.*, 14(9), 563 (1946).
3. W. B. White, et al., "Chemical Equilibrium in Complex Mixtures," *J. Chem. Phys.*, 14(9), 563 (1946)
4. D. R. Atull, et al., "JANAF Thermochemical Table, 1982 Supplement," *J. Phys. Chem. Ref. Data*, 11, 695 (1982).
5. I. Barin, et al., "Thermodynamic Properties of Inorganic Substance," Springer-Verlag, Berlin (1977).
6. B. S. Hemingway, et al., "Thermodynamic Properties of Selected Minerals in the System Al_2O_3 - CaO - SiO_2 - H_2O at 298.15^oK and 1 bar (10 Pascals) Pressure and at High Temperature," U.S. Geological Survey Bulletin 1544 (1982).
7. D. D. Wagman, et al., "Selected Values of Chemical Thermodynamic Properties," U.S. NBS Technical note 270-3/8 (1968-1981).
8. A. K. Sarkar, et al., "Longevity of Borehole and Shaft Sealing Materials: Thermodynamic Properties of Cements and Related Phases Applied to Repository Sealing," ONWI 201 (1982).
9. R. C. Weast, et al., "CRC Handbook of Chemistry and Physics; 65th Edition," CRC Press, Inc., Boca Raton, Florida (1984).
10. W. L. Robert, et al., "Encyclopedia of Minerals," Van Nostrand Reinhold Company, New York (1974).
11. J. D. Donnay, et al., "Crystal Data; 3rd Edition," U.S. Secretary of Commerce, Swarthmore, Pennsylvania (1978).
12. H. Stepfaen, et al., "Solubilities of Inorganic and Organic Compounds" Pergamon Press Book, New York (1963).
13. A. N. Neville, "Properties of Concrete; 3rd edition," Pitman (1981).