

Models of Cement-Water Interaction and a Compilation of Associated Thermodynamic Data

January, 2000

JAPAN NUCLEAR CYCLE
DEVELOPMENT INSTITUTE

本資料の全部または一部を複写・複製・転写する場合は、下記にお問い合わせください。

〒319-1194 茨城県那珂郡東海村大字村松4-33
核燃料サイクル開発機構 東海事業所
運営管理部 技術情報室

Inquiries about copyright and reproduction should be addressed to :
Technical Information Section,
Administration Division,
Tokai Works,
Japan Nuclear Cycle Development Institute
4-33 Muramatsu, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1194
Japan

© 核燃料サイクル開発機構 (Japan Nuclear Cycle Development Institute)
2000

Models of Cement-Water Interaction and a Compilation of Associated Thermodynamic Data

David Savage¹⁾, K Lemke²⁾, Hiroshi Sasamoto³⁾
Masahiro Shibata³⁾, Randolph C Arthur⁴⁾, Mikazu Yui³⁾

Abstract

Modelling approaches that have been proposed for cement-water system are reviewed in this report, and relevant supporting thermodynamic data are compiled. The thermodynamic data include standard molal thermodynamic properties of minerals and related compounds comprising cements, and equilibrium constants for associated hydrolysis reactions. Similar data for minerals that are stable in hyperalkaline geologic environments (e.g., zeolites) are also included because these minerals could be formed as hyperalkaline fluids emanating from cementitious materials in a repository for radioactive wastes interact with the surrounding host rock. Standard molal properties (i.e., standard molal Gibbs free energies and enthalpies of formation and standard molal entropies), and/or equilibrium constants for associated hydrolysis reactions, are included for:

- cement minerals and related compounds (Reardon, 1992; Glasser et al., 1999)
- calcium-silicate hydrate minerals (Sarkar et al., 1982), and
- zeolites (calorimetric and estimated values from various sources)

All these data are accepted at face value, and it is therefore cautioned that the data, considered as a whole, may not be internally consistent. It is also important to note that the accuracy of these data have not been evaluated in the present study.

Several models appropriate for cement-water systems have been proposed in recent years. Most are similar in the sense that they represent empirical fits to laboratory data for the CSH gel-water system, and therefore not thermodynamically defensible. An alternative modeling approach based on thermodynamic principles of solid-solution behavior appropriate for CSH gel has recently been proposed, however. It is reviewed in the present study, and evaluated in relation to experimental results obtained by JNC on cement-water interactions.

The solid-solution model is based upon a thermodynamically- and structurally-justifiable description of CSH gel in terms of a non-ideal solid-solution of portlandite and calcium silicate

end-member components. Miscibility gap and solubility data for the two end-members have been employed using the computer code "MBSSAS" to investigate solubility behaviour for the solid-solution. A Lippmann phase diagram constructed using MBSSAS was used to input data to PHREEQC to calculate fluid compositional data in equilibrium with the gel solid-solution. A comparison of fluid compositions calculated with the gel solid-solution model with those available in the literature for the CSH gel-water system show good agreement.

The CSH gel solid-solution model was then used to simulate the results of JNC leaching tests using the PHREEQC software. Due to inadequacies of the PHREEQC code, it was necessary to input the CSH gel solid-solution as discrete "portlandite" and "calcium silicate" end-members with variable solubility in accordance with the Lippmann phase diagram. CSH gel solid-solution alone was considered to simulate the behaviour of OPC.

The CSH gel solid-solution model provide a reasonable fit to the JNC OPC leachate data, but there were discrepancies with the experimental data for fluid leachate volumes between 10,000 and 30,000 ml. An alternative modeling approach (Berner, 1992) provided a better overall fit to the JNC data than the solid-solution model.

Re-evaluation of the CSH gel model with respect to possible variations in end-member miscibility and solubility behaviour, together with a better representation of the overall cement system (inclusion of phases other than CSH gel) is anticipated to produce a better fit of modelled and experimental data. Further development of the both the CSH gel solid-solution model and cement-leaching simulation software (PHREEQC) is recommended to predict the evolution of cement pore fluid composition with time.

The Maquarin natural analogue site is a suitable site for the examination of the mechanisms and processes associated with cementitious repositories. The evidence at Maquarin will be useful to test the applicability of the CSH gel model under hyperalkaline conditions in future.

-
- 1) Quintessa, Ltd., Nottingham, UK
 - 2) University of Bristol, Bristol, UK
 - 3) Japan Nuclear Cycle Development Institute Tokai Works, Tokai-Mura, Ibaraki, Japan
 - 4) Monitor Scientific, LLC., Denver, Colorado, USA

セメント-水反応に係わるモデルおよびセメント系鉱物の熱力学データ
(研究報告)

David Savage¹⁾, K Lemke²⁾, 笹本 広³⁾
柴田雅博³⁾, Randolph C Arthur⁴⁾, 油井三和³⁾

要 旨

本報告書では、セメント-水反応に係わるモデルのレビューおよび収集したセメント系鉱物の熱力学データについて報告する。本報告書でまとめた熱力学データには、鉱物およびセメントを構成する化合物の標準モル熱力学特性、関連する水和反応の平衡定数を含む。また、高アルカリ性環境下で安定な鉱物（例えば、沸石など）についても同様にデータ整備を行った。これらの鉱物は、放射性廃棄物処分場におけるセメント系材料から流出する高アルカリ性溶液と処分場周辺の岩盤との反応の結果生成すると考えられる。

標準モル特性（すなわち、生成標準モルギブス自由エネルギー、生成標準モルエンタルピー、標準モルエントロピー）、関連する水和反応の平衡定数については、以下の文献による。

- ・セメント鉱物および関係する混合物 (Reardon, 1992; Glasser ほか, 1999)
- ・カルシウム-珪酸水和鉱物 (Sarkar ほか, 1982)
- ・沸石 (熱量測定の数値, 様々なデータからの推定値)

これらの全データは、個々の値としてとらえるべきものであり、データ全体としての内部整合性はとれていないかもしれない点に注意すべきである。また、本報告の中では、これら個々のデータの精度については評価していない点も留意する必要がある。

近年、セメント-水系における幾つかの適切なモデルが提案されている。これらのモデルの多くは、CSHゲル-水系の室内実験データへの経験的な適合を示すものであり、熱力学的に正当化されているものではない。一方、近年、CSHゲルに適した固溶体挙動の熱力学的理論に基づいたモデル化手法が提案されている。この手法については、本報告書の中でレビューすると共に、JNCが行ったセメント-水反応に係わる実験結果と比較することにより検証した。

固溶体モデルは、CSHゲルをポルトランダイトとカルシウム-珪酸塩を端成分組成とした非理想固溶体として表現する熱力学的・構造的に妥当なモデルである。2つの端成分の混和

性の違いや溶解度は、固溶体の溶解挙動を調べるためのコンピュータコードである「MBSSAS」を用いて求めた。MBSSAS を用いて作られた Lippmann 相図は、ゲルの固溶体と平衡にある溶液組成を計算する PHREEQC へのデータを入力するために用いられた。ゲルの固溶体モデルで計算された溶液組成と C S Hゲル-水系に係わる文献の実験データはよく一致している。

次に、PHREEQC を用いて C S Hゲルの固溶体モデルにより、JNC が行ったセメント-水反応試験の結果をシミュレートした。PHREEQC コードの不完全さのため、Lippmann 相図に従って、種々の溶解度積をもつ別々の「ポルトランドイト」や「カルシウム-珪酸塩」を端成分として C S Hゲルを入力する必要がある。普通ポルトランドセメント (OPC) の挙動をシミュレートするにあたり、本報告書では、C S Hゲルの固溶体のみを考慮した。

C S Hゲルの固溶体モデルは、JNC が実施した普通ポルトランドセメントの浸出試験結果にほぼ一致した。但し、浸出液の(累積)体積が 10,000~30,000 ml にかけての実験データには一致しなかった。代替モデル (Berner モデル; Berner, 1992) は、固溶体モデルよりも JNC の実験データをよりよく近似できた。

セメントシステムの全体像に関するよりよい概念 (C S Hゲル以外の固相も考慮する等) を構築するとともに、端成分の混和性や溶解度の変化幅に関して C S Hゲルモデルを再評価することでモデルと実験値のよりよい一致を生むことが期待される。今後、セメント空隙水の時間変化を予測するため、C S Hゲルの固溶体モデルやセメントの浸出挙動をシミュレートするためのソフトウェアの開発を行っていく必要がある。

Maquarin ナチュラルアナログサイトは、セメント材料を使用する処分場で生ずるプロセスやメカニズムを調べる上で適切なサイトである。Maquarin サイトで得られる知見は、今後、高アルカリ環境下での C S Hゲルモデルの妥当性を検討する上で有効になるであろう。

-
- 1) Quintessa, Ltd., Nottingham, UK
 - 2) University of Bristol, Bristol, UK
 - 3) Japan Nuclear Cycle Development Institute Tokai Works, Tokai-Mura, Ibaraki, Japan
 - 4) Monitor Scientific, LLC., Denver, Colorado, USA

Table of Contents

1	Introduction.....	1
2	Objectives.....	2
3	Cement Minerals and Related Compounds.....	3
4	Calcium Silicate Hydrate Minerals.....	6
5	Zeolites.....	7
6	Cement-Groundwater Interaction Models.....	9
6.1	CSH Gel Behaviour.....	9
6.2	Thermodynamic Models of CSH Gel.....	10
6.2.1	Atkinson <i>et al.</i> model.....	11
6.2.2	Glasser <i>et al.</i> model.....	11
6.2.3	Berner model.....	12
6.2.4	Reardon model.....	13
6.3	An alternative model for CSH gel behaviour.....	13
6.3.1	Construction of a Lippmann Diagram for the CSH gel-H ₂ O System.....	16
6.3.2	Verification of the CSH Gel Solid-Solution Model.....	18
6.4	Application of the CSH Gel Solid-Solution Model to JNC Cement Leach Tests.....	21
6.5	Evaluation of the CSH Gel Solid-Solution Model and Recommendations.....	23
7	Evidence from Natural Systems.....	25
8	Conclusions.....	27
9	References.....	28

1 Introduction

Cement and concrete are likely to be used extensively in any repository for long-lived intermediate level radioactive wastes in Japan. Because of the long-lived nature of some of the radioactive wastes to be disposed of in an ILW/TRU repository, it is desirable that hyperalkaline pore fluid conditions are also maintained in the long-term (in excess of 10^4 years). Elevated pH conditions are a function of the solubility and mass of pH-controlling solids within the cement, their interactions with aqueous species in groundwater saturating and flowing through the repository, and the rate of flow of groundwater through the system. The principal cement phase believed to be controlling pH in the long-term (at timescales relevant to performance assessment) is calcium silicate hydrate (CSH) gel. Consequently, it is necessary to have an understanding of how CSH gel interacts with water and to have a sound mechanistic and thermodynamically rigorous model of its behaviour.

Several models appropriate for cement-water systems have been proposed in recent years, but all are similar in the sense that they represent empirical fits to laboratory data for the CSH gel-water system, and are therefore not thermodynamically defensible. An alternative, thermodynamically-rigorous solid-solution model for CSH gel has been published recently, however, and it is evaluated in the present study. This model is based upon a thermodynamically- and structurally-justifiable description of CSH gel in terms of a non-ideal solid-solution of portlandite and calcium silicate end-member components. Miscibility gap and solubility data for the two end-members are employed using the computer code "MBSSAS" to investigate solubility behaviour for the solid-solution. In this approach, a Lippmann phase diagram constructed using MBSSAS is used to input data to geochemical models of aqueous-speciation behavior, such as PHREEQC, to calculate fluid compositional data in equilibrium with the gel solid-solution.

Thermodynamic data supporting chemical models of cement-water interaction are also compiled in this report. The data are taken at face value from several sources, including data recommended by Reardon (1992) and Glasser *et al.* (1999) for cement minerals and related compounds (Section 3), data for calcium-silicate hydrate minerals from Sarkar *et al.* (1982) (Section 4), and calorimetric and estimated thermodynamic data from several sources for zeolite minerals (Section 5). Proposed approaches for modelling cement-water systems are briefly reviewed in Section 6, where the approach noted above is also summarized and tested using relevant experimental data generated by JNC¹.

¹ The Japan Nuclear Cycle Development Institute (JNC) was established in 1998, and is responsible for many of the repository R&D functions formerly assigned to the Power Reactor and Nuclear Fuel Development Corporation (PNC).

2 Objectives

The objective of this report is to summarize modeling approaches that have been proposed for cement-water systems, and to compile relevant supporting thermodynamic data from literature sources. Relevant thermodynamic data include standard molal thermodynamic properties of minerals and related compounds comprising cements, and equilibrium constants for associated hydrolysis reactions. Similar data for minerals that are stable in hyperalkaline geologic environments (e.g., zeolites) may also be important because these minerals could be formed as hyperalkaline fluids emanating from cementitious materials in a repository for ILW/TRU wastes interact with the surrounding host rock. All the thermodynamic data compiled in this report are accepted at face value. It is therefore cautioned that the data, considered as a whole, may not be internally consistent. It is also cautioned that the accuracy of the data have not been evaluated in the present study.

Because models that have been proposed in recent years for cement-water systems are not thermodynamically defensible, an alternative modeling approach that is based on thermodynamic principles of solid-solution behavior appropriate for CSH gel is also described in the present study. The model is evaluated in relation to experimental results obtained by JNC on cement-water interactions.

3 Cement Minerals and Related Compounds

Thermodynamic data that can be used to model cement chemistry and cement pore water evolution are compiled in Table 3_1, based on reports by Reardon (1990, 1992). Reardon bases his approach on the Pitzer ion-interaction model for calculation of activity coefficients at high ionic strengths. A variable composition model for CSH gel is developed based on data reported by Gartner and Jennings (1987). The following expressions are used to calculate solution parameters in equilibrium with the CSH gel phase (see Section 6):

$$\left(\frac{Ca}{Si}\right)_{CSH} = 0.88 + 0.03 \exp^{0.513R}$$

$$-\text{Log}K_{SP} = 9.044 - 0.568R + 0.193R^2$$

where $R = \log (a_{Ca^{2+}} / a_{H_4SiO_4(aq)})$ and K_{SP} refers to the dissolution reaction of CSH gel.

An alternative dataset for cement minerals and solids (Table 3_2) is available in a recent compilation produced by Professor F. Glasser and colleagues at the University of Aberdeen (Glasser *et al.*, 1999). For the most part, these are data derived experimentally at the University of Aberdeen over the past 10 years under contract to the UK Department of the Environment (*e.g.*, Atkins *et al.*, 1991). The report describing these data is not yet available, however.

Table 3_1: Thermodynamic data for cement minerals and related compounds at 25°C, 1 bar (Reardon, 1992)

Substance/Mineral Name	Reaction	log K_r
Mg(OH) ₂ /brucite	$\text{Mg(OH)}_2 = \text{Mg}^{2+} + 2\text{OH}^-$	-10.88
Ca(OH) ₂ /portlandite	$\text{Ca(OH)}_2 = \text{Ca}^{2+} + 2\text{OH}^-$	-5.19
Ca ₆ Al ₂ O ₆ (SO ₄) ₃ .32H ₂ O/ ettringite	$\text{Ca}_6\text{Al}_2\text{O}_6(\text{SO}_4)_3.32\text{H}_2\text{O} = 6\text{Ca}^{2+} + 2\text{Al(OH)}_4^- + 3\text{SO}_4^{2-} + 4\text{OH}^- + 26\text{H}_2\text{O}$	-43.94
SiO ₂ .2H ₂ O/amorph. silica	$\text{SiO}_2.2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$	-2.70
CaO.Al ₂ O ₃ .CaCO ₃ .11H ₂ O/ Ca-carboaluminate	$\text{CaO}.Al_2\text{O}_3.CaCO_3.11\text{H}_2\text{O} = 2\text{Ca}^{2+} + 2\text{Al(OH)}_4^- + \text{CO}_3^{2-} + 7\text{H}_2\text{O}$	-19.54
3CaO.Al ₂ O ₃ .CaCl ₂ .10H ₂ O/ Friedel's salt	$3\text{CaO}.Al_2\text{O}_3.CaCl_2.10\text{H}_2\text{O} = 4\text{Ca}^{2+} + 2\text{Al(OH)}_4^- + 2\text{Cl}^- + 4\text{OH}^- + 4\text{H}_2\text{O}$	-31.62
Mg ₄ Si ₆ O ₁₅ (OH) ₂ .6H ₂ O/ sepiolite	$\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2.6\text{H}_2\text{O} + 3\text{H}_2\text{O} = 4\text{Mg}^{2+} + 6\text{H}_3\text{SiO}_4^- + 2\text{OH}^-$	-55.31
Al(OH) ₃ /gibbsite	$\text{Al(OH)}_3 + \text{OH}^- = \text{Al(OH)}_4^-$	-0.90
CaCO ₃ /calcite	$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-8.41
CaSO ₄ .2H ₂ O/gypsum	$\text{CaSO}_4.2\text{H}_2\text{O} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	-4.58
K ₂ SO ₄ /arcanite	$\text{K}_2\text{SO}_4 = 2\text{K}^+ + \text{SO}_4^{2-}$	-1.78
MgCO ₃ .3H ₂ O/ nesquehonite	$\text{MgCO}_3.3\text{H}_2\text{O} = \text{Mg}^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O}$	-5.12
CaMg(CO ₃) ₂ /dolomite	$\text{CaMg(CO}_3)_2 = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$	-17.08
2CaO.Al ₂ O ₃ .8H ₂ O/C ₂ AH ₃	$2\text{CaO}.Al_2\text{O}_3.8\text{H}_2\text{O} = 2\text{Ca}^{2+} + \text{Al(OH)}_4^- + 2\text{OH}^- + 3\text{H}_2\text{O}$	-13.75
3CaO.Al ₂ O ₃ .6H ₂ O/C ₃ AH ₆	$3\text{CaO}.Al_2\text{O}_3.6\text{H}_2\text{O} = 3\text{Ca}^{2+} + 2\text{Al(OH)}_4^- + 4\text{OH}^-$	-23.13
NaCl/halite	$\text{NaCl} = \text{Na}^+ + \text{Cl}^-$	1.57
Ca ₄ Cl ₂ (OH) ₆ .13H ₂ O/ Ca-oxychloride	$\text{Ca}_4\text{Cl}_2(\text{OH})_6.13\text{H}_2\text{O} = 4\text{Ca}^{2+} + 2\text{Cl}^- + 6\text{OH}^- + 13\text{H}_2\text{O}$	-15.25
Mg ₂ Cl(OH) ₃ .4H ₂ O/ Mg/oxychloride	$\text{Mg}_2\text{Cl(OH)}_3.4\text{H}_2\text{O} = 2\text{Mg}^{2+} + \text{Cl}^- + 3\text{OH}^- + 4\text{H}_2\text{O}$	-15.96
K ₂ Ca(SO ₄) ₂ .H ₂ O/ syngenite	$\text{K}_2\text{Ca(SO}_4)_2.H_2\text{O} = 2\text{K}^+ + \text{Ca}^{2+} + 2\text{SO}_4^{2-} + \text{H}_2\text{O}$	-7.45
K ₃ Na(SO ₄) ₂ /glaserite	$\text{K}_3\text{Na(SO}_4)_2 = 3\text{K}^+ + \text{Na}^+ + 2\text{SO}_4^{2-}$	-3.80
Ca ₄ Al ₂ O ₆ SO ₄ .12H ₂ O/ monosulphate	$\text{Ca}_4\text{Al}_2\text{O}_6\text{SO}_4.12\text{H}_2\text{O} = 4\text{Ca}^{2+} + 2\text{Al(OH)}_4^- + \text{SO}_4^{2-} + 4\text{OH}^- + 6\text{H}_2\text{O}$	-29.25
Na ₃ (HCO ₃)CO ₃ .2H ₂ O/ trona	$\text{Na}_3(\text{HCO}_3)\text{CO}_3.2\text{H}_2\text{O} = 3\text{Na}^+ + \text{HCO}_3^- + \text{CO}_3^{2-} + 2\text{H}_2\text{O}$	-1.04
NaHCO ₃ /nahcolite	$\text{NaHCO}_3 = \text{Na}^+ + \text{HCO}_3^-$	-0.40
xCaO.SiO ₂ .xH ₂ O/CSH (x = Ca/Si ratio)	$x\text{CaO}.SiO_2.x\text{H}_2\text{O} + \text{H}_2\text{O} = x\text{Ca}^{2+} + \text{H}_3\text{SiO}_4^- + (2x - 1)\text{OH}^-$	see Sec. 6

Table 3_2: Thermodynamic data for cement minerals and related compounds at 25°C, 1 bar (Glasser *et al.*, 1999)

Substance/Mineral Name	Reaction or Standard Properties			log <i>K_r</i>
	$\Delta_f H^\circ$ (kcal mol ⁻¹)	$\Delta_f G^\circ$ (kcal mol ⁻¹)	S° (cal K ⁻¹ mol ⁻¹)	
Ca ₃ Al ₂ SiO ₈ .4H ₂ O/katoite	-111.9	-	-	
	3Ca ²⁺ + 2Al ³⁺ + H ₄ SiO ₄ + 8H ₂ O - 12H ⁺ = Ca ₃ Al ₂ SiO ₈ .4H ₂ O			69.37 ^a
Ca(OH) ₂ /portlandite	Ca ²⁺ + 2H ₂ O = Ca(OH) ₂ + 2H ⁺			22.815 ^a
Mg ₂ (OH) ₃ Cl.4H ₂ O/ Mg-oxychloride	2Mg ²⁺ + Cl ⁻ + 7H ₂ O = Mg ₂ (OH) ₃ Cl.4H ₂ O + 3H ⁺			26.06 ^a
Mg ₄ Si ₆ O ₁₅ (OH) ₂ .6H ₂ O/ sepiolite	4Mg ²⁺ + 6H ₄ SiO ₄ + H ₂ O = Mg ₄ Si ₆ O ₁₅ (OH) ₂ .6H ₂ O + 8H ⁺			34.0a
MgSO ₄ .7H ₂ O/ epsomite	12.0	-	-	
	Mg ²⁺ + SO ₄ ²⁻ + 7H ₂ O = MgSO ₄ .7H ₂ O			-2.13 ^a
Mg ₄ Al ₂ O ₇ .10H ₂ O/ hydrotalcite	4Mg ²⁺ + 2Al ³⁺ + 17H ₂ O = Mg ₄ Al ₂ O ₇ .10H ₂ O + 14H ⁺			75.44 ^a
Ca ₆ Al ₂ (OH) ₁₂ (SO ₄) ₃ .26H ₂ O/ ettringite	-80.32	-	-	
	6Ca ²⁺ + 2Al ³⁺ + 3SO ₄ ²⁻ + 38H ₂ O = Ca ₆ Al ₂ (OH) ₁₂ (SO ₄) ₃ .26H ₂ O + 12H ⁺			55.223 ^a
Ca ₄ Al ₂ (OH) ₁₂ SO ₄ .6H ₂ O/ monosulphate	-120	-	-	
	4Ca ²⁺ + 2Al ³⁺ + SO ₄ ²⁻ + 18H ₂ O = Ca ₄ Al ₂ (OH) ₁₂ SO ₄ .6H ₂ O + 12H ⁺			71.36 ^a
Ca ₆ Al ₂ O ₆ Cl ₆ .xH ₂ O/ chloroettringite	6Ca ²⁺ + 2Al ³⁺ + 6Cl ⁻ + 36H ₂ O = Ca ₆ Al ₂ O ₆ Cl ₆ .xH ₂ O + 12H ⁺			56.84 ^a
Ca ₄ Al ₂ O ₆ CO ₃ .10H ₂ O/ monocarboaluminate	4Ca ²⁺ + 2Al ³⁺ + CO ₃ ²⁻ + 17H ₂ O = Ca ₄ Al ₂ CO ₃ .10H ₂ O + 12H ⁺			69.89 ^a
K ₂ SO ₄ / arcanite	5.7	-	-	
	2K ⁺ + SO ₄ ²⁻ = K ₂ SO ₄			-1.78 ^a
MgCO ₃ .3H ₂ O/nesquehonite	Mg ²⁺ + CO ₃ ²⁻ + 3H ₂ O = MgCO ₃ .3H ₂ O			-5.26 ^a
NaHCO ₃ /nahcolite	8.03	-	-	
NaCl/ halite	2.2	-	-	
	Na ⁺ + Cl ⁻ = NaCl			1.57 ^a
Ca ₂ Al ₂ SiO ₇ .8H ₂ O/ gehlenite hydrate	2Ca ²⁺ + 2Al ³⁺ + H ₄ SiO ₄ + 11H ₂ O = Ca ₂ Al ₂ SiO ₇ .8H ₂ O + 10H ⁺			49.67 ^a
Ca ₉ Si ₆ O ₁₈ H ₂ (OH) ₈ .6H ₂ O/ jennite	-187.0	-	-	
	9Ca ²⁺ + 6H ₄ SiO ₄ + 8H ₂ O = Ca ₉ Si ₆ O ₁₈ H ₂ (OH) ₈ .6H ₂ O + 18H ⁺			147.1 ^a
NaOH	Na ⁺ + H ₂ O = NaOH + H ⁺			20.9 ^a
KOH	K ⁺ + H ₂ O = KOH + H ⁺			15.852 ^a
Ca ₃ Al ₂ Si ₂ O ₈ (OH) ₄ /hibschite	-87.0	-	-	
CaK ₂ (SO ₄) ₂ .H ₂ O/syngenite	Ca ²⁺ + 2K ⁺ + 2SO ₄ ²⁻ + H ₂ O = CaK ₂ (SO ₄) ₂ .H ₂ O			-7.45 ^a
Ca ₄ Al ₂ Cl ₂ O ₆ .10H ₂ O/ Friedel's salt	4Ca ²⁺ + 2Al ³⁺ + 2Cl ⁻ + 16H ₂ O = Ca ₄ Al ₂ Cl ₂ O ₆ .10H ₂ O + 12H ⁺			72.04 ^a
Ca ₄ Al ₂ (SO ₄) _{0.5} Cl.12H ₂ O/ Kuzel's salt	4Ca ²⁺ + 2Al ³⁺ + Cl ⁻ + 0.5SO ₄ ²⁻ + 18H ₂ O = Ca ₄ Al ₂ (SO ₄) _{0.5} Cl.12H ₂ O + 12H ⁺			71.94 ^a
Ca ₄ O ₃ Cl ₂ .16H ₂ O/ Ca-oxychloride	4Ca ²⁺ + 2Cl ⁻ + 19H ₂ O = Ca ₄ O ₃ Cl ₂ .16H ₂ O + 6H ⁺			68.75 ^a

^a - Log *K* formulated using the Davies equation for activity coefficient calculation.

4 Calcium Silicate Hydrate Minerals

Thermodynamic data for the calcium silicate hydrate (CSH) minerals, hillebrandite, afwillite, foshagite, xonotlite, tobermorite, gyrolite, and okenite (Table 4_1), were derived from the compilation produced by Sarkar *et al.* (1982). The data for the CSH minerals quoted in Sarkar *et al.* (1982) are, in turn, derived from the work of Mchedlov-Petrossian (1972), which are calculated data. According to Sarkar *et al.* (1982), Mchedlov-Petrossian's data agree satisfactorily with available experimental data, *e.g.*, Newman (1956). The data for CSH minerals from Sarkar *et al.* (1982) are included in other compilations of this type, *e.g.*, the thermodynamic database accompanying EQ3/6 (Wolery, 1992).

Substance/Mineral Name	Formation from the Elements		
	$\Delta_f H^\circ$ (kcal mol ⁻¹)	$\Delta_f G^\circ$ (kcal mol ⁻¹)	S° (cal K ⁻¹ mol ⁻¹)
Ca ₂ SiO ₄ .1.17H ₂ O/hillebrandite	-637.15	-592.9	38.4
Ca ₃ Si ₂ O ₇ .3H ₂ O/afwillite	-1143.2	-1052.95	74.6
Ca ₄ Si ₃ O ₁₀ .1.5H ₂ O/foshagite	-1439.99	-1347.9	78.95
Ca ₆ Si ₆ O ₁₈ .H ₂ O/xonotlite	-2396.7	-2259.4	121.3
Ca ₅ Si ₆ O ₁₇ .5.5H ₂ O/11 Å tobermorite	-2556.3	-2361.45	146.15
Ca ₅ Si ₆ O ₁₇ .5.5H ₂ O/14 Å tobermorite	-2911.25	-2647.3	193.15
Ca ₅ Si ₆ O ₁₇ .5.5H ₂ O/9 Å tobermorite	-2375.0	-2215.0	122.65
Ca ₂ Si ₃ O ₈ .2.5H ₂ O/gyrolite	-1175.85	-1085.65	64.0
CaSi ₂ O ₅ .2H ₂ O/okenite	-750.3	-686.4	40.9

Table 4_1: Thermodynamic data for CSH minerals and solids at 25°C, 1 bar (Sarkar *et al.*, 1982)

5 Zeolites

Thermodynamic data for zeolites (Table 5_1) are derived both from calorimetric (analcime, laumontite, leonhardite, mesolite, mordenite, natrolite, scolecite, wairakite, and yugawaralite) and modeling (chabazite, clinoptilolite, epistilbite, erionite, heulandite, phillipsite, and stilbite) studies. The calorimetric data were obtained either by G. K. Johnson and co-workers at the Argonne National Laboratory, Illinois, USA (Johnson *et al.*, 1982, 1983, 1992), or by Kiseleva *et al.* (1996a,b). Bowers and Burns (1990) noted that several of the data from Johnson and co-workers (particularly laumontite, stilbite and chabazite) resulted in the lack of stability fields at low temperature.

Modeled data were either derived from the paper by Bowers and Burns (1990) {chabazite, clinoptilolite, epistilbite, heulandite, phillipsite, and stilbite} or that by Chermak and Rimstidt (1989) {erionite}. Bowers and Burns (1990) used the approach described by Chen (1975) to estimate Gibbs free energies of formation at 25°C where these data are missing for various zeolites. This method involves the summation of several sets of components (oxides, silicates, etc.) which are then fitted with an exponential curve which asymptotically approaches a low value defining the standard molal Gibbs free energy of formation. An error less than 6% is anticipated for this method. Chermak and Rimstidt (1989) use a different method to estimate Gibbs free energies and enthalpies of formation for zeolites. They adopt the method of "summation of polyhedral contributions" described by Hazen (1988) and use multiple linear regression techniques to assess the contribution of various oxide components to the zeolite thermodynamic constants.

Modeled data for zeolites are also reported by La Iglesia and Aznar (1986), but are not incorporated into data tables presented here.

Table 5_1: Thermodynamic data for zeolites at 25°C, 1 bar

Substance/Mineral Name	Formation from the Elements			Ref.*
	$\Delta_f H^\circ$ (kcal mol ⁻¹)	$\Delta_f G^\circ$ (kcal mol ⁻¹)	S° (cal K ⁻¹ mol ⁻¹)	
Na _{0.96} Al _{0.96} Si _{2.04} O ₆ ·H ₂ O/analcite	-790.1	-737.6	54.2	92JOH/82JOH
CaAl ₂ Si ₄ O ₁₂ ·6H ₂ O/chabazite	-1866.8	-1712.6	-	90BOW
Na _{0.56} K _{0.98} Ca _{1.5} Mg _{1.23} Al _{6.7} Fe _{0.3} Si ₂₉ O ₇₂ ·22H ₂ O/ clinoptilolite	-9811.9	-9057.8	-	90BOW
CaAl ₂ Si ₆ O ₁₆ ·5H ₂ O/epistilbite	-2234.8	-2065.2	-	90BOW
KAlSi ₃ O ₈ ·3H ₂ O/erionite	-	-1065.7	-	89CHE
CaAl ₂ Si ₇ O ₁₈ ·6H ₂ O/heulandite	-2519.9	-2326.6	-	90BOW
CaAl ₂ Si ₄ O ₁₂ ·4H ₂ O/laumontite	-1733.0	-1601.1	116.0	96aKIS
CaAl ₂ Si ₄ O ₁₂ ·3.5H ₂ O/leonhardite	-1698.7	-1573.3	110.2	96bKIS
Na _{0.676} Ca _{0.657} Al _{1.990} Si _{3.01} O ₁₀ ·2.647H ₂ O/mesolite	-1424.8	-1321.1	86.8	92JOH/83JOH
Ca _{0.289} Na _{0.361} Al _{0.94} Si _{5.06} O ₁₂ ·3.468H ₂ O/mordenite	-1614.8	-1493.2	116.3	92JOH
Na ₂ Al ₂ Si ₃ O ₁₀ ·2H ₂ O/natrolite	-1370.1	-1274.1	86.0	92JOH/83JOH
Na ₂ Al ₂ Si ₅ O ₁₄ ·5H ₂ O/Na-phillipsite	-2003.5	-1851.4	-	90BOW
K ₂ Al ₂ Si ₅ O ₁₄ ·5H ₂ O/K-phillipsite	-2025.5	-1871.5	-	90BOW
CaAl ₂ Si ₅ O ₁₄ ·5H ₂ O/Ca-phillipsite	-2010.1	-1860.6	-	90BOW
CaAl ₂ Si ₃ O ₁₀ ·3H ₂ O/scolecite	-1449.1	-1341.3	87.8	92JOH/83JOH
NaCa ₂ Al ₅ Si ₁₃ O ₃₆ ·14H ₂ O/stilbite	-5247.5	-4833.6	-	90BOW
CaAl ₂ Si ₄ O ₁₂ ·2H ₂ O/wairakite	-1588.6	-1483.8	95.8	96aKIS
CaAl ₂ Si ₆ O ₁₆ ·4H ₂ O/yugawaralite	-2163.3	-2008.3	145.7	96aKIS

* 90BOW- Bowers and Burns R.G. (1990); 89CHE- Chermak and Rimstidt (1989); 82JOH- Johnson *et al.* (1982); 83JOH - Johnson *et al.* (1983) ; 92JOH- Johnson *et al.* (1992); 96aKIS- Kiseleva *et al.* (1996a); 96bKIS- Kiseleva *et al.* (1996b).

6 Cement-Groundwater Interaction Models

Cement and concrete are likely to be used extensively in any repository for long-lived intermediate level radioactive wastes in Japan. The hyperalkaline pore fluid conditions maintained by cement/concrete systems is perceived to be beneficial for the isolation of radioactive wastes because of:

- minimization of metal (particularly iron/steel) corrosion;
- minimization of the solubility of certain radionuclide-bearing solids;
- minimization of microbial activity in the repository.

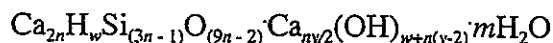
Because of the long-lived nature of some of the radioactive wastes to be disposed of in an ILW/TRU repository, it is desirable that hyperalkaline pore fluid conditions are also maintained in the long-term (in excess of 10^4 years).

Elevated pH conditions are a function of the solubility and mass of pH-controlling solids within the cement (*e.g.*, portlandite, calcium silicate hydrate gel), their interactions with aqueous species in groundwater saturating and flowing through the repository, and the rate of flow of groundwater through the system. It follows therefore, that understanding the chemical interactions of cements with groundwaters is fundamental to the understanding of repository evolution. The principal cement phase believed to be controlling pH in the long-term (at timescales relevant to performance assessment) is calcium silicate hydrate (CSH) gel. This gel may constitute 50-70 volume % of Ordinary Portland Cement (OPC) [Mindess and Young, 1981]. It is necessary to have an understanding of how CSH gel interacts with water and have a sound mechanistic and thermodynamically rigorous model of its behaviour.

JNC are carrying out a programme of laboratory cement leach tests and computer modelling to be able to develop a thermodynamic model for CSH gel. The modelling activities are reviewed, and alternative approaches evaluated, in this section.

6.1 CSH Gel Behaviour

CSH gel is a product of the hydration of tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$) and dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$) in the cement clinker. CSH gel does not have a fixed chemical composition and has a variable Ca/Si ratio, from approximately one, to two, or higher. It is a near-amorphous material, but can be considered to have a "degenerate clay structure" [Mindess and Young, 1981], by which is meant that it can be thought to have a layered structure, consisting of sheets of calcium silicate with interlayer calcium ions and water. Richardson and Groves (1993) have proposed a general model of CSH gel as:



which is based on a disordered layer structure with "dreierketten" silicate chains of length $3n - 1$ in solid solution with variable amounts of $\text{Ca}(\text{OH})_2$. The simplest silicate end-

member composition is tobermorite-like CSH, such as $\text{Ca}_2\text{H}_2\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ (with $n = 1$, $w = 2$, and $m = 3$).

At solid Ca/Si ratios > 1 , CSH gel dissolves incongruently in water with aqueous Ca concentrations being much higher than those of Si. The extent of incongruent dissolution behaviour increases with the Ca/Si ratio of the solid. Ca-rich CSH gel (Ca/Si > 2) equilibrates with aqueous solutions of very high Ca/Si ratio ($> 10,000$), whereas low Ca/Si gel (Ca/Si ≤ 1) coexists with an aqueous phase with a Ca/Si ratio < 1 . Despite the non-stoichiometric dissolution behaviour, there is good evidence that dissolution behaviour is driven by thermodynamic equilibrium. Greenberg *et al.* (1960) were the first to conclude that CSH gel with CSH ratio > 1 is essentially a solid solution of $\text{Ca}(\text{OH})_2$ in a low Ca/Si ratio calcium silicate component. From a structural and aqueous chemical perspective therefore, there is good evidence that CSH gel can be described by a binary non-ideal solid-solution.

6.2 Thermodynamic Models of CSH Gel

Two types of model have been proposed to explain the behaviour of CSH gels from a thermodynamic perspective:

1. The first approach relies upon solubilities in the system $\text{CaO-SiO}_2\text{-H}_2\text{O}$ being recalculated to unique solubility products raised to fractional powers as a function of the Ca/Si ratio [Glasser *et al.*, 1988]. Unfortunately this approach is not consistent with the law of mass action, which requires that molecular compounds are formed via chemical reactions which necessitate non-fractional stoichiometric coefficients. Also, non-fractional stoichiometric coefficients are required to maintain electroneutrality of aqueous solutions (ionic charges are integers according to atomic theory). This model is otherwise appealing because non-constant solubility products are used to fit parameters describing experimental data in the system $\text{CaO-SiO}_2\text{-H}_2\text{O}$.
2. The second approach utilises the Gibbs-Duhem equation, which at constant pressure and temperature can be applied to each phase in the 3-component system $\text{CaO-SiO}_2\text{-H}_2\text{O}$:

$$X_C^i d\mu_C^i + X_S^i d\mu_S^i + X_H^i d\mu_H^i = 0,$$

where μ_i are chemical potentials in each respective component. An expression such as the following can be written to relate the Ca/Si ratio of the solid to the chemical composition of the aqueous phase:

$$R_{C/S} = \frac{X_C^S}{X_S^S} = \frac{-d\mu_S}{d\mu_C} \frac{1 - m_S^{aq} R_{H/S}}{55.51} + \frac{m_C^{aq} R_{H/S}}{55.51}$$

where $R_{H/S}$ is the molar H_2O/SiO_2 ratio of the solid and m denotes units of molality. The major disadvantage of this approach is that it does not incorporate any structural information on CSH gel, such as non-ideal mixing behaviour or miscibility gaps.

Models used to explain CSH gel behaviour in radioactive waste disposal have tended to be of the first type. The more important of these are those of:

- Atkinson *et al.* (1987);
- Glasser *et al.* (1988);
- Berner (1992);
- Reardon (1990, 1992).

Each of these models will be discussed briefly below.

6.2.1 Atkinson *et al.* model

Atkinson *et al.* (1987) developed an empirical model to describe the evolution of cement pore fluid chemistry based on the following:

- at Ca/Si ratios of the solid > 0.833, stable solids are assumed to be portlandite and “tobermorite”;
- at Ca/Si ratios of the solid < 0.833, stable solids are assumed to be silica and “tobermorite”.

Solubility functions were derived (Table 6.2.1_1) from the experimental data of Greenberg and Chang (1965) to describe cement pore fluid evolution with time. This model has no strict thermodynamic basis, nor is it related to the structural or chemical behaviour of CSH gel.

Ca/Si Range	Model Solids	Solubility Function
Ca/Si < 0.833	SiO ₂ (silica) 0.833CaOSiO ₂ ·0.917H ₂ O (tobermorite)	$\Delta_r G_x^\circ = 1\ 643\ 708\ \text{J/mol}$ L _{sx} = 0 J/mol A _{sx} = 2 000 J/mol L _{px} = 9 000 J/mol A _{px} = -29 000 J/mol x = tobermorite s = silica p = portlandite
0.833 < Ca/Si	CaOH ₂ (portlandite) 0.833CaOSiO ₂ ·0.917H ₂ O (tobermorite)	as above

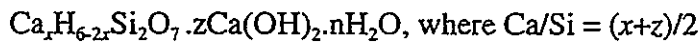
Table 6.2.1_1: Model solids and their solubility relationships for various Ca/Si ratios of the cement composition for the Atkinson *et al.* (1987) model.

6.2.2 Glasser *et al.* model

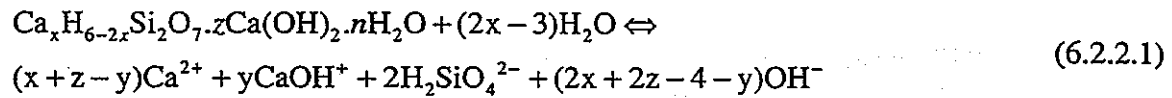
Glasser *et al.* (1988) proposed a compositional model for CSH gel which takes account of:

- its poor crystallinity;
- Si is present as dimers;
- Ca(OH)₂ is easily leached from the gel until the Ca/Si ratio reaches 1.25, whereupon it becomes difficult to remove.

The following chemical formula for CSH gel with Ca/Si in the range 0.9 to 1.4 was used:



A dissolution reaction was written as follows:



with the following solubility product:

$$K_{sp} = [\text{Ca}^{2+}]^{(x+z-y)} [\text{CaOH}^+]^y [\text{H}_2\text{SiO}_4^{2-}]^2 [\text{OH}^-]^{(2x+2z-4-y)} \quad (6.2.2.2)$$

K_{sp} values were written for Eqn. (6.2.2.2) using laboratory experimental data from the literature (Table 6.2.2_1). For CSH gels with higher Ca/Si ratios an expression for Ca(OH)₂ solubility would have to be incorporated into Eqn. (6.2.2.2).

Although this model pays greater attention to gel composition and behaviour, it suffers from a lack of thermodynamic rigour, requiring fractional coefficients in the mass action relationship, and is again an empirical fit to laboratory experimental data.

Ca/Si Range	Model Solids	Solubility Function
0.8 < Ca/Si < 1.7	$\text{Ca}_x\text{H}_{6-2x}\text{Si}_2\text{O}_7 \cdot z\text{Ca}(\text{OH})_2$	$\log K = -9.478(\text{Ca/Si}) - 7.54$

Table 6.2.2_1: Model solid and its solubility relationships for CSH gel for the Glasser *et al.* (1988) model.

6.2.3 Berner model

The Berner model (Berner, 1992) is the most commonly applied model of cement pore fluid evolution in studies of radioactive waste disposal. Like other CSH solubility models, the incongruent dissolution behaviour of CSH gel is represented by considering the solubility of two separate solids with variable solubility products. This approach was deemed to be necessary because of the limitations of speciation-solubility computer codes such as PHREEQE which are unable to treat solid-solution explicitly. Different model solids are used for different Ca/Si ratios of the gel (Table 6.2.3_1). Berner developed

quadratic equations to describe experimental measurements of CSH gel behaviour and incorporated these into his model. Berner identified three different regimes of CSH gel behaviour:

- $0 < \text{Ca/Si} < 1$: silica and CaH_2SiO_4 (both with variable solubility products);
- $1 < \text{Ca/Si} \leq 2.5$: portlandite $[\text{Ca}(\text{OH})_2]$ and CaH_2SiO_4 (portlandite with variable solubility product);
- $\text{Ca/Si} > 2.5$: portlandite $[\text{Ca}(\text{OH})_2]$ and CaH_2SiO_4 (both fixed solubility products).

Berner defined the term "apparent solubility product" to describe the variable solubility products used in the model. Again this model is thermodynamically questionable, utilising variable solubility products for solids of fixed composition. Although available experimental data are accurately reproduced, it has no rigorous thermodynamic basis.

Ca/Si Range	Model Solids	Solubility Function
0	SiO_2	$\log K = -2.70$
$0 < \text{Ca/Si} < 1$	SiO_2	$\log K = -2.04 + \frac{0.792}{\text{Ca/Si} - 1.2}$
	CaH_2SiO_4	$\log K = -8.16 - \frac{1 - \text{Ca/Si} \left(\frac{0.78 + 0.792}{\text{Ca/Si} - 1.2} \right)}{\text{Ca/Si}}$
$1 < \text{Ca/Si} \leq 2.5$	$\text{Ca}(\text{OH})_2$	$\log K = -4.945 - \frac{0.328}{\text{Ca/Si} - 0.85}$
	CaH_2SiO_4	$\log K = -8.16$
$\text{Ca/Si} > 2.5$	$\text{Ca}(\text{OH})_2$	$\log K = -5.15$
	CaH_2SiO_4	$\log K = -8.16$

Table 6.2.3_1: Model solids and their solubility relationships for various Ca/Si ratios of the cement composition for the Berner (1992) model.

6.2.4 Reardon model

Reardon recognised that CSH gel is not a pure phase with a unique solubility product and therefore used the data of Gartner and Jennings (1987) to produce a quadratic fit of solution composition versus the Ca/Si ratio of the solid [Reardon 1990, 1992]. Reardon presents two quadratic equations to describe both the solubility and Ca/Si ratio of CSH gel based upon these CSH solubility measurements. The Reardon model is summarised in Table 6.2.4_1.

An innovation which Reardon introduced was to use Pitzer coefficients to calculate activities of aqueous species. On the debit side, Reardon's model for CSH gel does not account explicitly for its solid-solution behaviour and is an empirical fit to laboratory experimental data.

Ca/Si Range	Model Solids	Solubility Function
$\left(\frac{Ca}{Si}\right)_{CSH} = 0.88 + 0.03e^{0.513R}$	$XCaO \cdot SiO_2 \cdot xH_2O$	$-\log K = 9.044 - 0.568R + 0.193R^2$

Table 6.2.4_1: Model solid and its solubility relationships for CSH gel for the Reardon (1992) model.

6.3 An alternative model for CSH gel behaviour

All of the above models provide reasonable fits to the available experimental data for CSH gel behaviour (as they should, since the models were constructed directly from the experimental data). It is difficult to promote one of these models over any other as being 'better' since they all rely essentially upon the same approach. However, the models are in no sense mechanistic and thus cannot be expected to simulate CSH gel behaviour under conditions outside those of the experiments used to condition the models. Also, there is no real thermodynamic basis for the utilisation of so-called "apparent solubility products". Kersten (1996) has highlighted these problems and has suggested an alternative model for CSH gel behaviour which will be considered in more detail here.

Kersten's thesis is that CSH gel can be treated as a solid-solution of variable composition and solubility, rather than as two discrete phases of fixed composition with variable solubility products. According to Kersten, the structure of CSH gel can be described by a solid-solution with a silicate end-member of general composition $Ca_2H_2Si_2O_7 \cdot 3H_2O$, and a calcium end-member represented by portlandite, $Ca(OH)_2$. Both these end-members are assumed to be congruently soluble. Kersten then writes mass action relationships for these two solids as follows, with a common cation, $CaOH^+$:

$$Ca_2H_2Si_2O_7 \cdot 3H_2O = [CaOH^+]^2 [H_3SiO_4^-]^2 = K_{CS}^2 \quad (6.3.1)$$

$$Ca(OH)_2 = [CaOH^+] [OH^-] = K_{CH} \quad (6.3.2)$$

where $[CaOH^+]$, $[H_3SiO_4^-]$ and $[OH^-]$ are the aqueous phase activities of $CaOH^+$, $H_3SiO_4^-$ and OH^- , "CS" is the calcium silicate end-member and "CH" is the portlandite end-member, and K_{CS} and K_{CH} are the equilibrium constants of the two reactions, respectively.

Kersten then applied solid-solution theory developed by Lippmann (1980) and Glynn and co-workers (Glynn and Reardon, 1990; Glynn *et al.*, 1990) to provide a description of the solubility behaviour of the CSH gel solid-solution. For the two gel end-members defined above (simplifying the composition of the silicate end-member), the following relationships hold:

$$[CaOH^+] [H_3SiO_4^-] = K_{CS} a_{CS} = K_{CS} X_{CS} \gamma_{CS} \quad (6.3.3)$$

$$[CaOH^+] [OH^-] = K_{CH} a_{CH} = K_{CH} X_{CH} \gamma_{CH} \quad (6.3.4)$$

where terms in square brackets are aqueous phase activities, a_{CH} and a_{CS} are the solid phase activities of CS and CH in the gel, X_{CS} and X_{CH} are mole fractions of CS and CH in the gel and γ_{CS} and γ_{CH} are activity coefficients for CS and CH in the gel.

Equations 6.3.3 and 6.3.4 can be added together to define a "total solubility product" constant, $\Sigma\Pi_{eq}$:

$$\Sigma\Pi_{eq} = K_{CS}a_{CS} + K_{CH}a_{CH} = K_{CS}X_{CS}\gamma_{CS} + K_{CH}X_{CH}\gamma_{CH} \quad (6.3.5)$$

and a "total solubility product" variable:

$$\Sigma\Pi = [CaOH^+][H_3SiO_4^-] + [OH^-] \quad (6.3.6)$$

Note that the $\Sigma\Pi_{eq}$ constant is dependent upon the composition of the solid-solution, whereas the $\Sigma\Pi$ variable is not. $\Sigma\Pi$ is analogous to the ion activity product of a pure solid phase.

Equation (6.3.5) defines the so-called "solidus curve" on a Lippmann phase diagram and can be calculated if the activity coefficients of the end-member solid-solution components are known.

Alternatively, $\Sigma\Pi_{eq}$ can be calculated from the activity fractions of the substituting ions in the aqueous phase to define Lippmann's so-called "solutus curve". The activity fractions (χ_{OH^-} and $\chi_{H_3SiO_4^-}$) are defined as:

$$\chi_{OH^-} = \frac{[OH^-]}{[OH^-] + [H_3SiO_4^-]} \quad (6.3.7)$$

and

$$\chi_{H_3SiO_4^-} = \frac{[H_3SiO_4^-]}{[OH^-] + [H_3SiO_4^-]} \quad (6.3.8)$$

Re-arranging Eqns. (6.3.3) and (6.3.4) in terms of X_{CS} and X_{CH} , adding the two equations together and using Eqns. (6.3.7) and (6.3.8) yields:

$$\Sigma\Pi_{eq} = \frac{1}{\frac{\chi_{OH^-}}{K_{CH}\gamma_{CH}} + \frac{\chi_{H_3SiO_4^-}}{K_{CS}\gamma_{CS}}} \quad (6.3.9)$$

Since γ_{CS} and γ_{CH} depend upon the solid-phase composition, the solutus equation is not strictly a function of the aqueous phase alone, except in the special situation of an ideal solid-solution series where $\gamma = 1$.

The above relationships can be used in a thermodynamically rigorous fashion to investigate the solubility behaviour of a CSH gel-water system.

6.3.1 Construction of a Lippmann Diagram for the CSH gel-H₂O System

The computer code 'MBSSAS' (Glynn, 1991) has been used to investigate solid-solution behaviour in the CSH gel-H₂O system. MBSSAS operates on an IBM-compatible personal computer and is freely available from the U.S. Geological Survey (*via* Pierre Glynn).

MBSSAS will calculate thermodynamic parameters for any solid-solution, requiring input data concerning the solubility products of the pure end-member components of the solid-solution, and any one of the following types of information:

- the location of miscibility gaps in the solid-solution;
- the location of spinodal gaps in the solid-solution;
- critical mixing points;
- information on alyotropic extrema;²
- Henry's law solid phase activity coefficients; or
- limiting distribution coefficients.

Output data consist of Lippmann phase diagrams, Roozeboom diagrams and distribution coefficient diagrams.

The description of the thermodynamic properties of a non-ideal solid solution requires knowledge of the excess free energy of mixing (G^E) of the solid-solution. MBSSAS uses a Guggenheim subregular solid-solution model (Guggenheim, 1937, 1952), as modified by Redlich and Kister (1948) and King (1969) to calculate free energies of mixing of the two components within the solid-solution. The Guggenheim approach has been used successfully to model the solubility data for a variety of binary carbonate, sulphate and oxide solid solutions (Glynn and Reardon, 1990). This model states that the excess free energy of mixing of a solid-solution, B_{1-x}C_xA, can be described as a function of composition by:

$$G^E = X_{BA} X_{CA} RT [\alpha_0 + \alpha_1 (X_{BA} - X_{CA}) + \dots] \quad (6.3.1.1)$$

² An alyotropic composition is defined as an intermediate composition for which a solid solution has a maximum or minimum solubility (Lippmann, 1980; Glynn, 1991).

where α_0 and α_1 are dimensionless fitting parameters, R is the gas constant and T is temperature ($^{\circ}\text{K}$). MBSSAS will calculate values for the α_0 and α_1 parameters from the input information concerning solid-solution miscibility gaps, *etc.* The free energy of mixing data are then used to calculate Lippmann's solidus, solutus and stoichiometric saturation curves.

To calculate a Lippmann diagram for the CSH gel-H₂O system, the following data (as described by Kersten, 1996) were used:

- Solid-solution end-members for the gel were assumed to be calcium silicate (CS) and portlandite (CH).
- Complete solid-solution in the C-S-H system is not known and the gel cannot be synthesised from salts with a Ca/Si ratio greater than 3 (Berner, 1992). In a solid solution between portlandite and Ca-silicate end-members, this implies no solid-solution beyond $X_{CH} = 0.67$. For input to MBSSAS, a miscibility gap between $X_{CH} = 0.67$ and $X_{CH} = 0.95$ was chosen (a value greater than 0.95 caused instability in MBSSAS calculations).
- Equilibrium constants chosen for the solubility of the two pure end-members [Eqns. (6.3.1) and (6.3.2)], K_{CS} and K_{CH} , were 1.6×10^{-8} and 10^{-4} , respectively.

Using these data, MBSSAS calculates dimensionless Guggenheim α_0 and α_1 parameters of -2.42 and 3.45, respectively. The Lippmann diagram calculated in this manner for the calcium silicate-portlandite solid-solution system is illustrated in Fig. 6.3.1_1.

A Lippmann diagram is analogous to phase diagrams for binary gas or liquid mixtures or solid/melt systems in that it consists of a solidus curve [defined by the total solubility product calculated using Eqn. (6.3.5)] and a solutus curve [defined by the activity ratio of aqueous species calculated using Eqn. (6.3.9)]. The solidus and solutus curves form a loop typical of other phase diagrams, which becomes wider as the difference between the solubility products of the pure end-members increases. Horizontal tie-lines (conodes) can be drawn between the solidus and solutus curves, tying together coexisting solid and aqueous phase compositions. Note that the solid phase is considered in terms of a mole fraction scale, whilst the aqueous phase is described by an activity fraction scale. In order to be able to plot aqueous phase compositions on a Lippmann diagram, distribution of species calculations (via a code such as PHREEQC) need to be carried out.

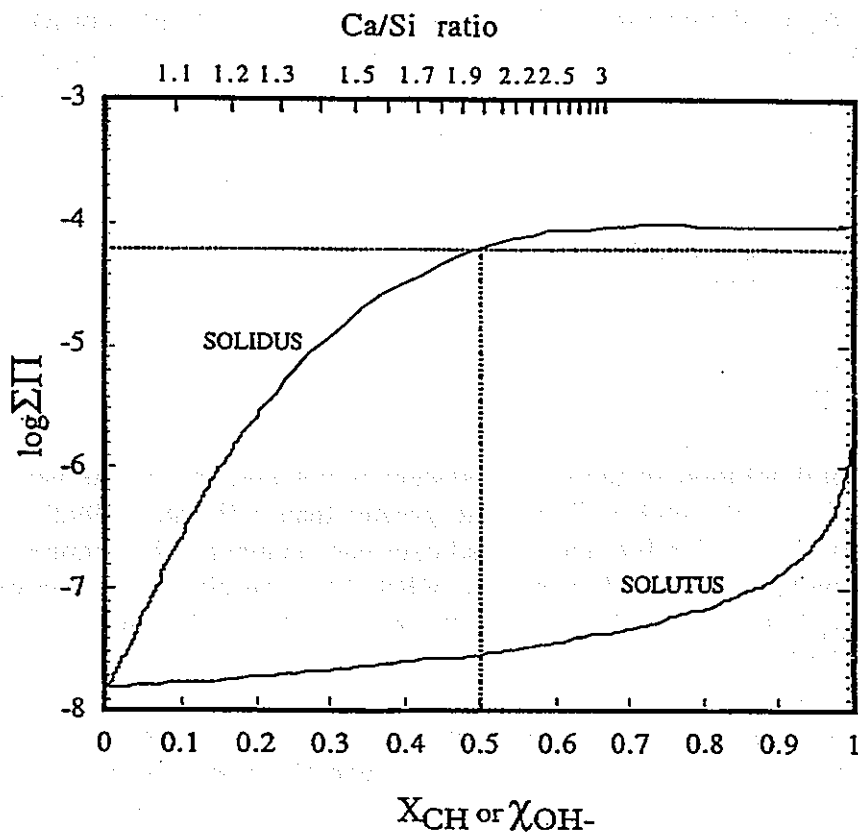


Figure 6.3.1_1: Lippmann diagram for the calcium silicate-portlandite binary system calculated using MBSSAS. Total solubility product values ($\Sigma\Pi_{eq}$) on the ordinate are plotted against two superimposed scales on the abscissa: X_{CH} refers to the mole fraction of portlandite in the solid phase and χ_{OH^-} refers to the activity fraction of OH^- in the aqueous phase ($[OH^-]/[OH^- + H_3SiO_4]$). The diagram consists of an upper solidus curve (plotted using X_{CH} and $\Sigma\Pi_{eq}$ values). These curves delineate the composition of the coexisting solid and fluid phase compositions at equilibrium with the calcium silicate-portlandite solid-solution. The equilibrium values of $\Sigma\Pi$ for the coexisting solid and aqueous compositions are related by the equilibrium constants for the dissolution of the two end-members calcium silicate ($\log K = -7.8$) and portlandite ($\log K = -4.0$), involving the calcium species $CaOH^+$ as a common cation. The asymmetric, non-ideal mixing behaviour is represented by a miscibility gap $0.95 > X_{CH} > 0.67$. Also shown for interest are tie-lines joining compositions of the solid and aqueous phases at equilibrium for a hypothetical $CH_{0.5}CS_{0.5}$ solid solution.

The composition of the aqueous phase is skewed heavily in favour of the more soluble end-member. From Fig. 6.3.1_1 it can be seen that a CSH gel solid solution consisting of 50% portlandite and 50% calcium silicate coexists with an aqueous phase which consists of roughly 100% of the OH^- anion and has a $\log \Sigma\Pi_{eq}$ value of -4.2. This highlights the non-stoichiometric dissolution behaviour of such a solid-solution.

6.3.2 Verification of the CSH Gel Solid-Solution Model

In order to test the applicability of the CSH gel solid-solution model, compositions of the aqueous phase coexisting with a CSH gel solid solution have been calculated using values of $\Sigma\Pi_{eq}$ derived from Fig. 6.3.1_1, and compared with solubility data for CSH gels compiled by Jennings (1986).

PHREEQC [Parkhurst, 1995] has been used to carry out these calculations. Since PHREEQC cannot explicitly deal with solid-solutions as input data, solid solution compositions derived from the Lippmann diagram were treated within PHREEQC as two discrete phases, calcium silicate and portlandite. However, instead of using equilibrium constants for the pure end-members, the following expressions were used, such that together, the $\Sigma\Pi_{aq}$ values from Figure 6.3.1_1 were satisfied:

$$[CaOH^+][H_3SiO_4^-] = K_{CS} X_{CS} \gamma_{CS} \quad (6.3.2.1)$$

$$[CaOH^+][OH^-] = K_{CH} X_{CH} \gamma_{CH} \quad (6.3.2.2)$$

Activity coefficients for the solid phase components used in Eqns. (6.3.2.1) and (6.3.2.2) were calculated using the α_0 and α_1 parameters derived from MBSSAS and the following expressions [Glynn and Reardon, 1990]:

$$\ln \gamma_{CS} = X_{CH}^2 [\alpha_0 - \alpha_1 (3X_{CS} - X_{CH})] = X_{CH}^2 [\alpha_0 - \alpha_1 (3 - 4X_{CH})] \quad (6.3.2.3)$$

$$\ln \gamma_{CH} = X_{CS}^2 [\alpha_0 + \alpha_1 (3X_{CH} - X_{CS})] = X_{CS}^2 [\alpha_0 + \alpha_1 (4X_{CH} - 1)] \quad (6.3.2.4)$$

The equilibrium constants calculated in this way for the different compositions of the gel solid-solution are presented in Table 6.3.2_1. Also presented in the table are fluid compositions in equilibrium with the gel compositions calculated using PHREEQC.

gel X_{CH}	$\log K_{CH}$	$\log K_{CS}$	pH	ΣCa	ΣSi	$CaOH^+$	$H_3SiO_4^-$	OH^-
0.67	-4.01	-8.97	12.45	0.020	5.2E-7	3.4E-3	3.2E-7	0.310
0.60	-4.05	-8.90	12.44	0.019	6.4E-7	3.2E-3	3.9E-7	0.027
0.55	-4.11	-8.83	12.42	0.018	8.0E-7	3.0E-3	5.0E-7	0.026
0.50	-4.19	-8.74	12.39	0.017	1.1E-6	2.7E-3	6.9E-7	0.025
0.45	-4.30	-8.64	12.35	0.015	1.6E-6	2.2E-3	1.0E-6	0.022
0.40	-4.45	-8.53	12.29	0.013	2.4E-6	1.8E-3	1.7E-6	0.020
0.35	-4.65	-8.41	12.22	0.011	4.0E-6	1.4E-3	2.9E-6	0.017
0.30	-4.89	-8.29	12.13	0.008	7.2E-6	9.5E-4	5.4E-6	0.014
0.25	-5.19	-8.18	12.03	0.006	1.4E-5	6.1E-4	1.1E-5	0.011
0.20	-5.56	-8.07	11.89	0.005	3.0E-5	3.5E-4	2.4E-5	0.008
0.15	-6.02	-7.98	11.73	0.003	7.0E-5	1.8E-4	5.9E-5	0.005
0.10	-6.58	-7.90	11.53	0.002	1.9E-4	7.8E-5	1.6E-4	0.003
0.05	-7.33	-7.84	11.24	0.001	6.1E-4	2.7E-5	5.4E-4	0.002
0.00	---	-7.80	11.04	0.001	1.1E-3	1.6E-5	1.0E-3	0.001

Table 6.3.2_1: Equilibrium constants for portlandite (CH) and Ca-silicate (CS) end-members of a CSH gel solid-solution input to PHREEQC for calculation of coexisting fluid compositions. Fluid compositions calculated by PHREEQC for gel compositions are also presented (in moles/litre).

The fluid compositions calculated using the CSH gel solid-solution model are plotted together with those summarised by Jennings (1986) for laboratory studies of CSH gel solubility in Fig. 6.3.2_1. As can be seen, there is a reasonable fit of the model data to those from laboratory studies of the CSH gel system. It should be emphasized that these experimental data were not employed in the calibration of the model and are a completely independent dataset. This provides confidence in the use of the model to simulate cement leaching experiments. However, the slight divergence in the trends between modelled and experimental data suggests that boundary conditions for the modelling (gel miscibility gap, solubility constants for the two end-members) could be re-evaluated to attempt to provide a better fit to the experimental data. These modifications were not attempted in the present study, but could be addressed in any further study of this type.

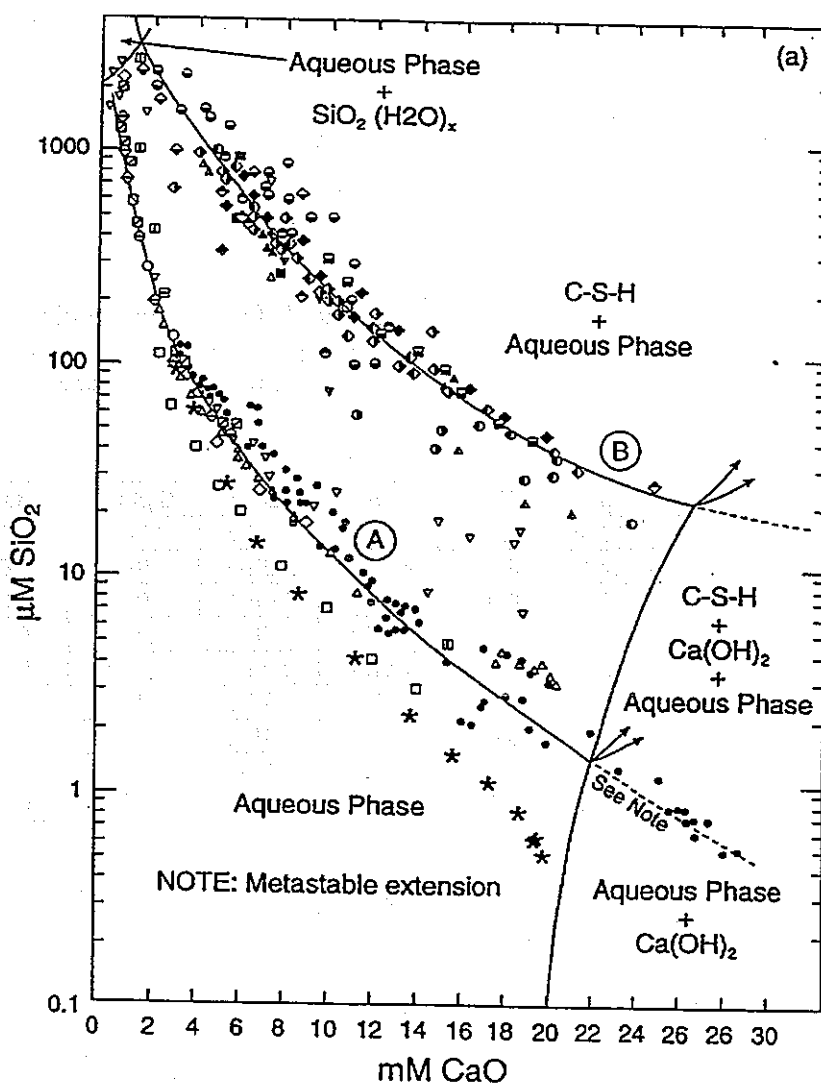


Figure 6.3.2_1: comparison of fluid phase compositions calculated for a CSH gel solid-solution model (starred data points) with those determined in laboratory CSH gel-water equilibration experiments as presented by Jennings (1986). Note the closeness of fit with data on "curve A" from Jennings. These data refer to gels synthesized from Ca(OH)_2 and silicic acid starting materials.

6.4 Application of the CSH Gel Solid-Solution Model to JNC Cement Leach Tests

Laboratory experiments have been carried out by JNC to investigate cement leaching. These data were to test the CSH gel solid-solution model described above. The experiments consisted of batch leaching of three different cement types with fresh water at room temperature in an inert atmosphere. Fluid/solid ratios (ml/g) of 1000:50 were used with periodic measurement of pH and fluid composition to monitor changing fluid composition with leachate volume. Cumulative leachate volumes of 70,000 ml were achieved in these tests. The leaching data for Ordinary Portland Cement (OPC) were used to test the CSH gel solid-solution model.

For the solid-solution model the following assumptions were made:

- The cement consisted solely of CSH gel, represented by portlandite and Ca-silicate gel end-members. The initial Ca/Si ratio of OPC was used to determine how much of each end-member was present in the starting material.
- PHREEQC was used to model the leaching of the cement. The leachate was assumed to be pure water. The initial solid composition consisted of 0.3329 moles of portlandite and 0.1664 moles of Ca-silicate (total 50 g) which was then "leached" using the "transport" function of PHREEQC. This transport function is a simple box model with no explicit hydrodynamic parameters such as dispersion included.
- The log K 's for the portlandite and Ca-silicate CSH gel end-members (from Table 6.3.2_1) were fixed over increments of X_{CH} until the Ca/Si ratio of the solid changed to the next incremental value (increments of 0.10 X_{CH} were used). For example, log K 's for portlandite and Ca-silicate were fixed for a range of gel composition of Ca/Si from 3.0 to 2.9 at the Ca/Si ratio of 2.95 ($X_{CH} \approx 0.65$). This "manual" adjustment of the log K values was necessary since PHREEQC does not include any direct means of equilibrating a solid-solution with an aqueous phase.

Output concerning the evolution of fluid composition and solid Ca/Si ratio with leachant volume was tabulated for plotting together with the JNC experimental data. Fluid compositional data generated in this manner have been compared with the results of the JNC leach tests in Fig. 6.4_1. For reference, results of simulations using the Berner model are also presented in this diagram.

From Fig. 6.4_1 it can be seen that:

- pH and Ca for the JNC experimental data, Berner model and solid-solution model are similar (pH \approx 12.5, Ca \approx 20 millimolal) up to approximately 10,000 ml leached and beyond 30,000 ml leached (pH \approx 11, Ca \approx 1 millimolal), but the solid-solution model calculates a higher pH and higher Ca concentration than both the Berner model and the JNC experimental data in the interval between these leachate volumes. The Berner

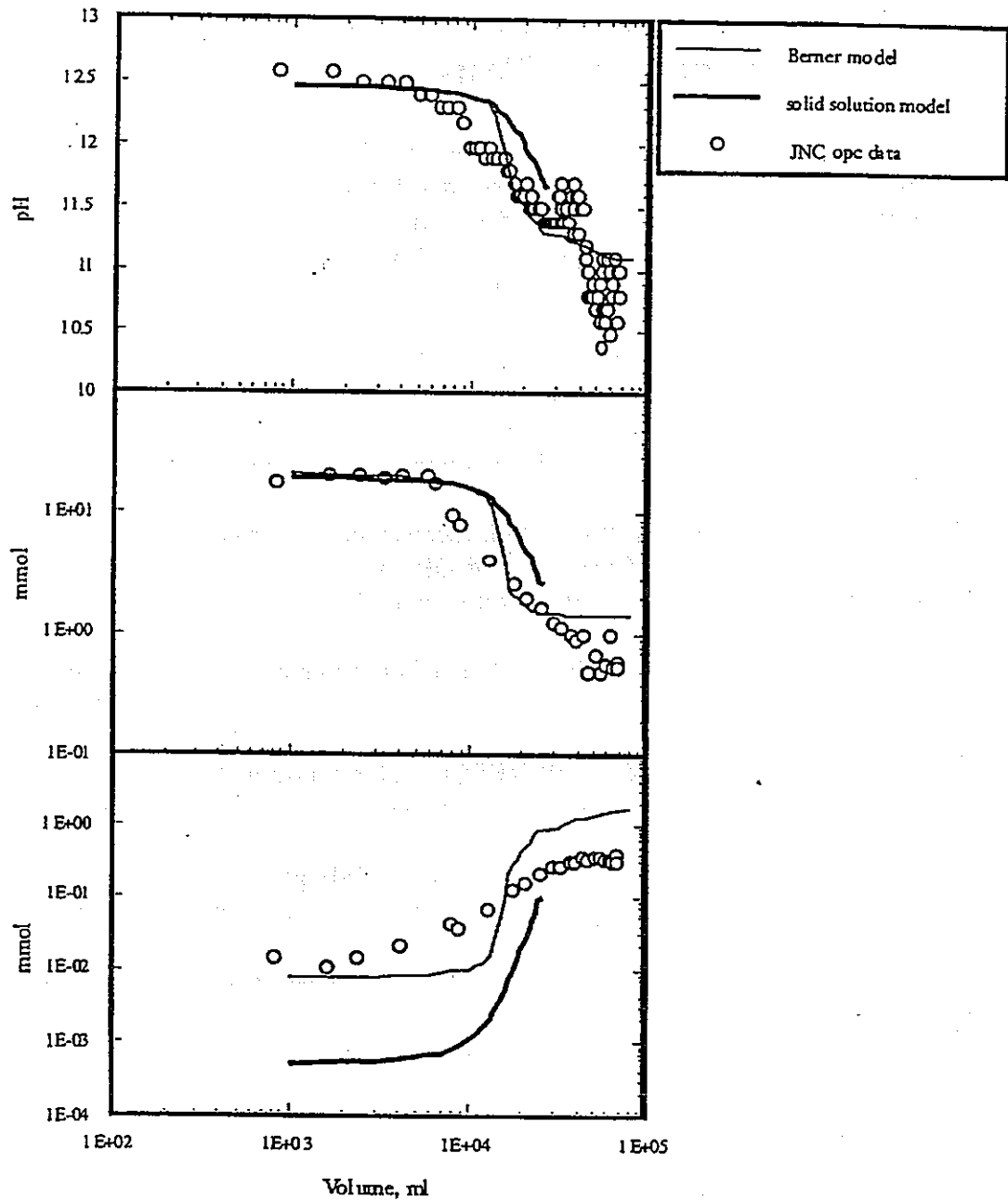


Figure 6.4_1: Comparison of the evolution of fluid phase compositions with leachate volume calculated for the CSH gel solid-solution model with those calculated using the Berner model and those measured in JNC cement leaching experiments.

model matches the experimental data more closely in this interval, albeit at a slightly higher pH and Ca concentration than the experimental data.

- Data for silicon are substantially different for the JNC experimental data, Berner model, and the solid-solution model. Each curve has a broad “S” shape with increasing leachate volume, but the curve of the “S” is much shallower for the experimental data compared with the two model simulations. The solid-solution

model estimates a silicon concentration of $\approx 10^{-6}$ molal up to 10,000 ml leached, whereas the JNC experimental data and the Berner model indicate Si concentrations of 10^{-5} molal. The Berner model simulation shows the steepest rise in Si concentration with leachate volume, from approximately 0.01 millimolal after 15,000 ml leached to 1 millimolal after 30,000 ml leached.

In addition, fluid phase compositions calculated by the solid-solution leachate model are compared with those derived by the Berner model in Fig. 6.4_2. It was not possible to extend the solid-solution model beyond a Ca/Si ratio less than unity. Although data for the two models are quite similar, for a given solid Ca/Si ratio the solid-solution model calculates a lower pH, and lower Ca and Si concentrations. pH is significantly lower for the solid-solution model as the Ca/Si ratio of the solid approaches unity. Also, at a Ca/Si ratio greater than 2, the solid-solution model calculates an aqueous phase silicon concentration approximately an order of magnitude lower than that of the Berner model.

6.5 Evaluation of the CSH Gel Solid-Solution Model and Recommendations

From the comparisons described above (Section 5) it can be concluded that representation of cement behaviour by a solid-solution model for CSH gel alone is apparently less accurate than currently-available models, such as that developed by Berner (1992). However, it should be noted that the solid-solution model considered CSH gel alone and

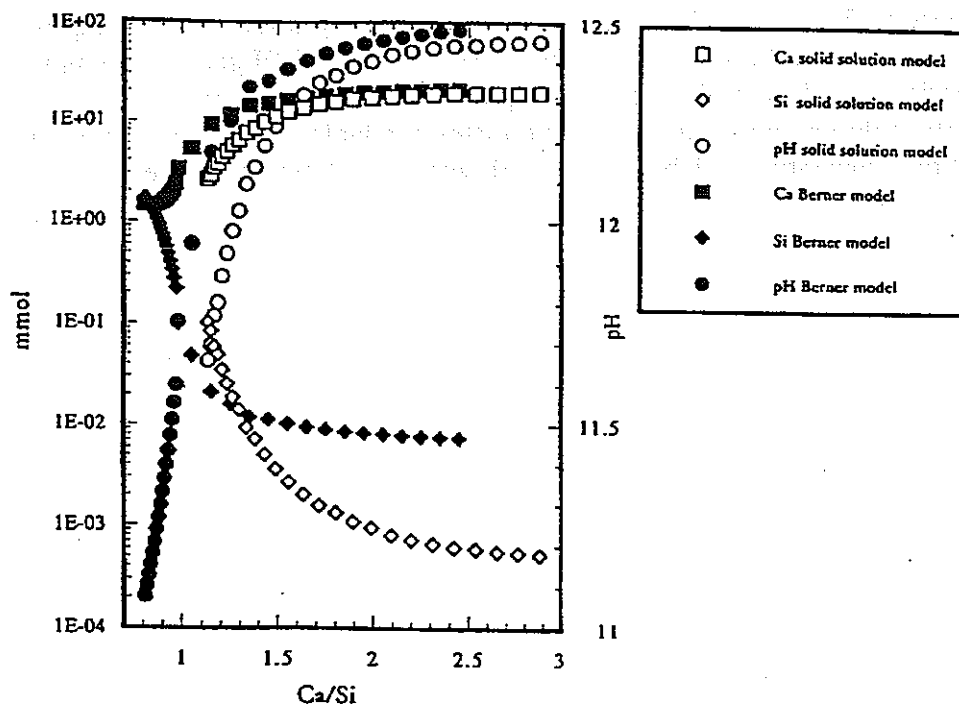


Figure 6.4_2: Comparison of the variation of fluid phase composition with Ca/Si ratio of the solid phase calculated for a CSH gel solid-solution model with that calculated using the Berner (1992) model.

did not include other solid phases to add greater realism to the simulation of the JNC cement-water experiments. The aim of the project reported here was to test the relevance of a solid-solution model for CSH gel, rather than develop a new model for cement as a whole. The similarity of the solid-solution model data to those experimental data obtained on CSH gels (Fig. 6.3.2_1) suggests that the solid-solution model is a good approximation of the CSH gel-water system which would argue for future addition of other phases to simulate more accurately the cement-water system. These additions to the model could be investigated in future studies of this type.

No refinement of the solid-solution model described by Kersten (1996) was attempted in the study reported here. Further development of the model to investigate sensitivity of the output data to parameters such as miscibility gap information and solubility data for pure end-members is recommended.

Application of the CSH gel solid-solution model was limited by the current capabilities of speciation-solubility codes such as PHREEQC. In this study it was not possible to define a CSH gel as a discrete solid-solution phase within PHREEQC. Instead, the gel was represented by two discrete end-members (portlandite and Ca-silicate) with solubility functions in accordance with an accurate thermodynamic representation of non-ideal solid-solution behaviour. Consequently, it was necessary to "manually" adjust the solubility data of the two end-members in accord with the changing Ca/Si ratio of the gel. Further development of PHREEQC, or the writing of specific software is recommended to facilitate solid-solution modelling.

As opposed to other currently available models for CSH gel behaviour, the solid-solution model developed by Kersten (1996) and described here, is thermodynamically rigorous, is based upon documented chemical and structural behaviour of CSH gel, is not empirically fitted to experimental data, and is thus extrapolatable to any chemical system. As it stands, this solid-solution model apparently simulates available cement leach experimental data less well than currently available models. However, with further refinement, a model of CSH gel behaviour with a thermodynamically-justifiable solid-solution basis is more likely to produce a defensible model of cement-water behaviour.

7 Evidence from Natural Systems

Natural analogue studies are useful to understand the long term phenomena that cannot be observed by laboratory experiments. The study of natural systems relevant to cementitious radioactive waste repositories has focussed on Maqarin, Jordan. Here, the natural combustion of bituminous limestones has resulted in the occurrence of cement clinker-type minerals and their hydration products. Hyperalkaline spring waters of pH 12.5 occur in dam foundation investigation adits and valley sides. Opportunity exists for the collection and analysis of the spring waters, and their interaction not only with limestones, but also with chert and basalt colluvial materials. The Maqarin analogue has been investigated since 1990, in three phases (Alexander et al., 1992; Linklater, 1998; Smellie, 1998), focussing on issues such as: water-rock interaction; trace element solubility and model testing; microbiology; colloid occurrence and stability; organics; and clay stability.

There is excellent detailed evidence for the reaction of a number of rock types (limestone, chert, basalt) with a Ca-OH-SO₄ fluid of elevated pH at Maqarin. Although these reactions are complex and highly variable, in general, a reaction sequence of the following can be observed where Ca-OH-SO₄ fluids initially contact limestones: carbonate, gypsum -> ettringite-thaumasite -> CSH gel -> zeolites. The reverse of this alteration sequence can be observed where fluids have already reacted appreciably with the impure limestones. These sequences are interpretable by reaction of hyperalkaline fluids with rocks containing aluminosilicate minerals and by considering how much rock the fluids have previously reacted with. Although there are limitations in the varieties of minerals contained within thermodynamic databases employed in geochemical and coupled reaction and flow models, the essential features of these mineral parageneses can be understood from theoretical geochemical considerations and by numerical simulations. The reaction sequences observed at Maqarin are directly relevant to understanding the reaction of evolved (i.e. calcium-dominated) hyperalkaline fluids with rocks, albeit with the understanding that the Maqarin groundwaters have particularly high sulphate contents, and that Maqarin rock types are aluminosilicate-poor (with the exception of the basalt colluvium). Unfortunately, these mineral parageneses tell us very little about the reaction of Na-K dominated cement pore fluids with rocks. The most hyperalkaline springs at Maqarin, the so-called 'Western Springs' contain levels of Na and K which are an order of magnitude less than those expected in 'early' cement pore fluids.

Evidence from Maqarin shows consistently that the interaction of calcium-dominated hyperalkaline fluids with limestones, chert and basalt decreases porosity (and probably permeability), ultimately sealing fractures where alteration is taking place. Age dating of one such fracture suggests that this occurs over 10-100 years. However, reactivation of fractures through tectonic/erosional activity has maintained spring activity in the Maqarin system over a 10⁵ year time period.

Wall rock alteration takes place within 0.5 to 4 mm of fractures at Maqarin. There is a zone of enhanced porosity immediately adjacent to the fracture and precipitation of a zone of calcite approximately 1 mm into the rock. This suggests that the rock matrix is initially available to the diffusion of aqueous species from a fluid-filled fracture, but that this

diffusion may be subsequently inhibited due to the filling of porosity in the matrix due to mineral precipitation.

There are no quantitative data available from Maqarin concerning radionuclide retardation, although evidence exists for the co-precipitation of U, Th, Se, Ni, Pb (up to 10's ppm) in zeolites, brucite, jennite and CSH gels.

Colloid abundances in groundwaters at Maqarin are low, of the order 10^4 ml⁻¹. However, the samples taken for colloid analysis at Maqarin may not be the most appropriate to assess potential maxima of colloid abundances in hyperalkaline systems. This is because Si concentrations in Maqarin hyperalkaline groundwaters are buffered at low levels (< 1 mg/l) by ettringite-thaumasite solubility. High silica concentrations can develop in pore fluids at elevated pH in the absence of Ca. These fluids may produce very high concentrations of colloids at pH fronts where they mix with groundwaters of lower pH.

Humic acids are absent from Maqarin groundwaters, but organic material in the limestones appears to be dissolved during alkaline alteration and re-precipitated at zones of porosity reduction in the rock matrix.

8 Conclusions

Currently available models to describe cement calcium silicate hydrate (CSH) gel-water behaviour are similar in that they are empirical fits to laboratory data for the CSH gel-water system. Non-stoichiometric dissolution behaviour is either represented by a solid phase with non-integer stoichiometric coefficients or two pure solid phases with "variable solubility products". Neither of these approaches is thermodynamically defensible.

An alternative, thermodynamically-rigorous solid-solution model for CSH gel has been described by Kersten (1996) and is the subject of the study reported here. This model is based upon a thermodynamically- and structurally-justifiable description of CSH gel in terms of a non-ideal solid-solution of portlandite and calcium silicate end-member components. Miscibility gap and solubility data for the two end-members have been employed using the computer code "MBSSAS" to investigate solubility behaviour for the solid-solution. A Lippmann phase diagram constructed using MBSSAS was used to input data to PHREEQC to calculate fluid compositional data in equilibrium with the gel solid-solution. A comparison of fluid compositions calculated with the gel solid-solution model with those available in the literature for the CSH gel-water system show good agreement.

The CSH gel solid-solution model was then used to simulate the results of JNC leaching tests using the PHREEQC software. Due to inadequacies of the PHREEQC code, the CSH gel solid-solution was input as discrete "portlandite" and "calcium silicate" end-members with variable solubility products in accordance with the Lippmann phase diagram. CSH gel solid-solution alone was considered to simulate the behaviour of OPC.

The CSH gel solid-solution model provided a reasonable fit to the JNC OPC leachate data, but there were discrepancies with the experimental data for fluid leachate volumes between 10,000 and 30,000 ml. The Berner model (Berner, 1992) provided a better overall fit to the JNC data than the solid-solution model.

Evaluation of the CSH gel model with respect to possible variations in end-member miscibility and solubility behaviour, together with a better representation of the overall cement system (inclusion of phases other than CSH gel) is anticipated to produce a better fit of modelled and experimental data. Further development of the both the CSH gel solid-solution model and cement-leaching simulation software (PHREEQC) is recommended to improve JNC's capability to predict the evolution of cement pore fluid composition with time.

The Maquarin natural analogue site is a suitable site for the examination of the mechanisms and processes associated with cementitious repositories. The evidence at Maquarin will be useful to test the applicability of the CSH gel model under hyperalkaline conditions in future.

9 References

- Alexander, W. R. (ed.) (1992). A natural analogue study of hyperalkaline groundwaters. I. Source term description and thermodynamic database testing, Nagra Technical Report, 91-10.
- Atkins, M., Glasser, F.P., Kindness, A. and Macphee, D.E. 1991. Immobilization of radwaste in cement based matrices. Solubility modelling of blended cement systems. UK Department of the Environment Report DoE/HMIP/RR/91/ 032.
- Atkinson, A., Hearne, J.A. and Knights, C.F. 1987. Aqueous chemistry and thermodynamic modelling of CaO-SiO₂-H₂O gels. UK Atomic Energy Authority Report AERE-R12548.
- Berner, U. 1992. Evolution of pore water chemistry during degradation of cement in a radioactive waste repository environment. *Waste Management*, 12, 201-219.
- Bowers, T.S. and Burns, R.G. 1990. Activity diagrams for clinoptilolite: susceptibility of this zeolite to further diagenetic reactions. *Am. Mineral.*, 75, 601-619.
- Chen, C-H. 1975. A method of estimation of standard free energies of formation of silicate minerals at 298.15 °K. *Am. J. Sci.*, 275, 801-817.
- Chermak J.A. and Rimstidt D. 1989. Estimating the thermodynamic properties of silicate minerals at 298 K from the sum of polyhedral contributions. *Am. Mineral.*, 74, 1023-1031.
- Gartner, E.M. and Jennings, H.M. 1987. Thermodynamics of calcium silicate hydrates and their solutions. *J. Am. Cer. Soc.*, 70, 743-749.
- Glasser, F.P., MacPhee, D.E. and Lachowski, E.E. 1988. Solubility modelling of cements: Implications for radioactive waste immobilisation. In *Scientific Basis for Nuclear Waste Management Vol XI*, (M.J. Apted and R.E. Westermann, eds.), Materials Research Society, 331-341.
- Glasser, F.P., Pedersen, J., Goldthorpe, K., Atkins, M., Tyrer, M., Bennett, D., Ross, D. and Quillin, K. 1999. The chemistry of blended cement and backfills intended for use in radioactive waste disposal. UK Environment Agency Report (in press).
- Glynn, P.D. 1991. MBSSAS: a code for the computation of Margules parameters and equilibrium relations in binary solid-solution aqueous-solution systems. *Computers and Geosciences*, 17, 907-966.
- Glynn, P.D. and Reardon, E.J. 1990. Solid-solution aqueous-solution equilibria: Thermodynamic theory and representation. *Am. J. Sci.*, 290, 164-201.

- Glynn, P.D., Reardon, E.J., Plummer, L.N. and Busenberg, E. 1990. Reaction paths and equilibrium end-points in solid-solution aqueous-solution systems. *Geochim. Cosmochim. Acta*, 54, 267-282.
- Greenberg, S.A. and Chang, T.N. 1965. Investigation of the colloidal hydrated calcium silicates: II Solubility relationships in the calcium oxide - silica - water system at 25 °C. *J. Phys. Chem.*, 69, 182-188.
- Greenberg, S.A., Chang, T.N. and Anderson, E. 1960. Investigation of colloidal hydrated calcium silicates. I. Solubility products. *J. Am. Cer. Soc.*, 64, 1151.
- Guggenheim, E.A. 1937. Theoretical basis of Raoult's law. *Transactions of the Faraday Society*, 33, 151-159.
- Guggenheim, E.A. 1951. *Mixtures*. Oxford University Press.
- Hazen, R.M. (1988) A useful fiction: Polyhedral modelling of mineral properties. *Am. J. Sci.*, 288-A, 242-269.
- Jennings, H.M. 1986. Aqueous solubility relationships for two types of calcium silicate hydrate. *J. Am. Cer. Soc.*, 69, 614-618.
- Johnson G.K., Tasker I.R., Flotow H.E., O'Hare P.A.G. and Wise W.S. 1992. Thermodynamic studies of mordenite, dehydrated mordenite, and gibbsite. *Am. Mineral.*, 77, 85-93.
- Johnson G.K., Flotow H.E. and O'Hare P.A.G. 1983. Thermodynamic studies of zeolites: Natrolite, mesolite and scolecite. *Am. Mineral.*, 68, 1134-1145.
- Johnson G.K., Flotow H.E., O'Hare P.A.G. and Wise W.S. 1982. Thermodynamic studies of zeolites: Analcime and dehydrated analcime. *Am. Mineral.*, 67, 736-748.
- Kersten, M. 1996. Aqueous solubility diagrams for cementitious waste stabilization systems. 1. The C-S-H solid-solution system. *Environ. Sci. Technol.*, 30, 2286-2293.
- King, M.B. 1969. *Phase Equilibrium in Mixtures*. Pergamon Press, New York.
- Kiseleva I., Navrotsky A., Belitsky I.A. and Fursenko B.A. 1996a. Thermochemistry and phase equilibria in calcium zeolites. *Am. Mineral.*, 81, 658-667.
- Kiseleva I., Navrotsky A., Belitsky I.A. and Fursenko B.A. 1996b. Thermochemistry of natural potassium sodium calcium leonhardite and its cation-exchanged forms. *Am. Mineral.*, 81, 668-675.
- La Iglesia, A. and Aznar, A.J. 1986. A method of estimating the Gibbs energies of formation of zeolites. *Zeolites*, 6, 26-29.

- Lippmann, F. 1980. Phase diagrams depicting aqueous solubility of binary mineral systems. *Neues Jahrb. Mineral. Abh.*, 139, 1-25.
- Linklater, C. M. 1998. A natural analogue study of cement-buffered, hyperalkaline groundwaters and their interaction with a repository host rock, UK Nirex Ltd., Report S/98/003.
- Mchedlov-Petrosian, O.P. (ed.) 1972. *Thermodynamics of silicates* (in Russian).
- Mindess, S. and Young, J.F. 1981. *Concrete*. Prentice-Hall, New Jersey, USA.
- Newman, E.S. 1956. Heats of formation of xonotlite, hillebrandite and foshagite. *Journal of Research of the National Bureau of Standards*, 57, 27-30.
- Parkhurst, D.L., Thorstenson, D.C. and Plummer, L.N. 1980. PHREEQE - a computer program for geochemical calculations, U.S. Geological Survey Water Resources Investigations Report 80-96.
- Parkhurst, D.L. 1995. User's guide to PHREEQC - a computer program for speciation, reaction-path, advective transport, and inverse geochemical calculations. U.S. Geological Survey Water Resources Investigations Report 95-4227.
- Reardon, E.J. 1990. An ion interaction model for the determination of chemical equilibria in cement/water systems. *Cement and Concrete Research*, 20, 175-192.
- Reardon, E.J. 1992. Problems and approaches to the prediction of the chemical composition in cement/water systems. *Waste Management*, 12, 221-239.
- Redlich, O. and Kister, A.T. 1948. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.*, 40, 345-348.
- Richardson, I.G. and Groves, G.W. 1993. The incorporation of minor and trace elements into calcium silicate hydrate (C-S-H) gel in hardened cement pastes. *Cement and Concrete Research*, 23, 131-138.
- Sarkar A.K., Barnes M.W., and Roy D.M. 1982. Longevity of borehole and shaft sealing materials: thermodynamic properties of cements and related phases applied to repository sealing: technical report. ONWI-201, prepared by The Pennsylvania State University for Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, OH.
- Smelie, J.A.T. 1998. Maquarin natural analogue study: Phase III, SKB Technical Report, TR-98-04.
- Wolery, T.J. 1992. EQ3/6, a software package for geochemical modeling of aqueous systems: package overview and installation guide (Version 7.0). Lawrence Livermore National Laboratory Report UCRL-MA-110662 PT I, Livermore, CA.