

## **Precipitate formation contributing to sump screens clogging of a nuclear power plant during an accident**

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### **Abstract**

For many years, IRSN has developed studies concerning chemical effects, which can occur during a loss of coolant accident (LOCA) on a Nuclear Power Plant, due to precipitate formation leading to an increase of head loss to sump screens. This increase can cause the loss of emergency core cooling system (ECCS) and of the containment spray system (CSS), which are two safety systems which ensure the accident mitigation.

These precipitates are formed by recombination of mineral species, which are released due to corrosion of immersed debris (particles of concrete, glass fiber insulation, piece of paint ...). PHREEQC software has been used to identify nature and mass of precipitates that can form during a LOCA.

This report presents the results of sensitivity studies carried out with PHREEQC. Chemical precipitate formation is studied as a function of several physical parameters, such as temperature, pH, nature and debris concentration. The optimal conditions in order to reduce the formation of precipitates are drawn from these calculations.

**Key words :** strainer clogging, precipitates, head loss, chemical effects, DBA nuclear accident.

### **1. Introduction**

In the case of a loss of coolant accident (LOCA) occurring to a nuclear pressurised water reactor (PWR), the emergency core cooling system (ECCS) and the containment spray system (CSS) are automatically activated according to some criteria. Water injection systems ensure going on with the reactor fuel cooling and spray allows decreasing the pressure and the temperature inside the containment reactor. The water is firstly pumped from a tank (IRWST) till minimal water level be reached. Then, both the ECCS and the CSS are connected with the containment bottom where the water is collected (sump). The water contains about 2500 ppm of boron acid and an amount of soda such the final pH solution is about 9.3.

For a LOCA, the shock wave from the pipe break (nominal parameters : 155 bar - 300°C) can be significant and the steam jet impact can damage several insulated structures around the pipe break. The main debris generated are : thermal insulation, principally made of glass fiber, paints and also concrete. Other additional debris (class of latent debris) such as dusts (iron oxides, etc.), present inside the containment nuclear reactor, can also be involved. A part of these debris are transported down to the filtration sump screens, located at the bottom of the containment ; these screens have been designed to retain the carried debris in order to prevent any damage caused by the debris circulation inside the recirculation pumps and the safety system lines.

A great part of these debris are agglomerated on these screens and are responsible for the sump plugging issue. Two examples can be given to illustrate this phenomenon. In 1979, gelatinous material was present on the sump screens after an accident which occurred to TMI-2 nuclear power plant ([Andreychek, 2004](#)) ; more recently, in July 1992, strainers on the suction side of the ECCS pump in Barsebäck NPP Unit 2 ([Pointner and al., 2005](#)) became partially plugged with mineral wool resulting from the opening of a safety valve leading to steam impinged on the thermally-insulated equipment and release of mineral wool in sump.

In order to better evaluate risk of sump screens clogging, and then loss of safety system, IRSN has launched experimental programs since 2000 ([Vicena and al., 2005](#)). The objective was to characterize the chemical effects due to debris corrosion in the containment under effects of solution composition and

temperature ; the chemical effects are caused by possible precipitation of species formed in the fibrous bed deposited on sump screens and the potential impact on head loss has been studied.

This program was divided in two parts. The first one was small-scale laboratory tests in order to determine debris dissolution kinetics. The second part consisted in two series of integral tests (ELISA and ELISA-babies loops) to measure head loss evolution as a function of time due to chemical effects in LOCA representative conditions. A specific model of head loss has been established. This model is based on mechanical properties evolution of the debris bed resulting from precipitate formation. In this objective, PHREEQC software has been used to predict nature and mass of precipitates that can be formed during a LOCA, from mineral species stemmed from debris corrosion.

This paper presents results of sensitivity studies on the impact of boundary conditions on mass of precipitates formed. The tool used to perform this sensitivity study is the PHREEQC software. At first, a brief description of the PHREEQC code is given, next the results obtained for a prototypical debris composition for a French 900 MWe PWR ; and finally a sensitivity study on the parameters is carried out to estimate the most significant sources of uncertainties.

## 2. PHREEQC code description

PHREEQC (Parkhurst and Appelo, 1999) is a software simulating chemical reactions and transport processes for natural waters and contaminated waters. Studied system is defined in the software with key words in the data blocs ; each one supplies a specific type of information.

PHREEQC allows knowing the possibility of precipitation or dissolution of a mineral compound.

This code calculates at equilibrium the distribution of mineral dissolved species and precipitates, present in aqueous solution, using a model of ion association. The main result is the determination of the saturation index (SI) for each stable mineral compound in solution ; this parameter allows to know if a mineral species can be formed or not (a precipitate formation is only possible if SI is positive). It is important to point out that kinetic is not considered.

## 3. Application of PHREEQC simulations to a 900 MWe French PWR reactor chemical conditions

Corrosion/dissolution of debris (glass fiber, concrete, paint, dust), in contact with sump solution, can be simulated with PHREEQC. System description is built in several steps. The first step consists in defining the corresponding aqueous solution composed of some mineral impurities, boric acid and sodium hydroxide. Next, the pH of the solution is fixed to the wished value. After that, each debris composition has to be defined to know the mineral species released by the corrosion effect. The result of the simulation is the amount of precipitate formed.

Initially, a constant temperature of 60°C is assumed. Each debris is independently studied to better assess their individual contribution to the global formation of precipitates.

### 3.1 Composition of the initial sump containment

Table 1 : Composition of water injected in containment vessel

Compounds	Content (ppm/w)
Chlorides (Cl <sup>-</sup> )	0.15
Fluorides (F <sup>-</sup> )	0.15
NaOH	0.40
Sulphate, SO <sub>4</sub> <sup>2-</sup>	0.15
Silica, SiO <sub>2</sub>	3.00
Al	0.10
Ca	0.10
Mg	0.10

Safety injection water contains about 2500 ppm in boric acid ( $H_3BO_3$ ). A sodium hydroxide tank allows fixing the pH solution to around 9.3, in order to prevent any gaseous iodine formation. Water content is defined in Table 1.

### 3.2 Debris composition

Three types of debris were used for experimental programs in VUEZ : BOURRE glass fibber, concrete and paint. The dusts were restricted to concrete particles. In the PHREEQC input file, each chemical formula of the debris has to be completed, as follows :

- for BOURRE glass fibber :



- for concrete :



- for paint :  $Na_{0.015}Al_{0.0141}Si_{0.0337}N_{0.1138}Ti_{0.1162}C_{0.2297}O_{1.1428}H_{2.2368}$

### 3.3 Assumptions

The exhaustive list of all potential precipitates is not retained, some precipitates were omitted because it was assumed that only amorphous  $SiO_2$  can be present in test conditions. It means that all the other precipitates with the  $SiO_2$  chemical formula (Quartz, Tridymite, Chalcedony, Cristobalite and Coesite), cannot exist in our solutions.

Due to kinetic limitations, Quartz and Tridymite are not taken into account because their crystallisation is highly unlikely at our time scale, i.e. a maximum of 3 months.

Literature data give us some indications to exclude some precipitates :

- Cristobalite is stable only at temperature higher than 1470°C, temperatures much higher than ours [30 °C-170°C] ;
- Coesite is generated during a metamorphism at very high pressure (300 bars), then its formation is improbable ;
- Chalcedony is a mixture of Quartz and Morganite, it is a crypto crystalline variety of Quartz. If Quartz is not formed, Chalcedony cannot be formed any longer.

It was estimated experimentally that 30%<sub>w</sub> of glass fibber are dissolved after being immersed in solution during one month (Mattei, to issue). To reach evolution of precipitate formation as a function of corrosion process, glass fibber dissolution was divided in ten steps, and the dissolution rate is assumed to be constant, i.e. 1%<sub>w</sub> per day, which means that kinetic of dissolution does not depend on the aqueous solution composition. In the same way, it has been considered from experimental program that 15%<sub>w</sub> of paint was dissolved after one-month immersion.

Moreover, according to experiments carried out at the Trencin University, concrete under fine powder form is instantaneously dissolved in the sodium-borate solution.

### 3.4 Precipitates formed during debris corrosion

In Table 2, for ELISA test conditions, i.e. for 550 L of solutions, are indicated the respective masses of the different debris involved.

Table 2 : Debris quantity in ELISA test conditions

Debris	Total insulation	Concrete	Dust	Paint
Mass (g)	836	46	46	46

PHREEQC gives the mass of precipitates formed as long as the corrosion process occurs. In Figure 1, the precipitates obtained are displayed in terms of mass ; four precipitates are predominant. At the beginning of

the dissolution, Tremolite, Tephroite and Stilbite represent about 95%<sub>w</sub> of precipitates, next Diopside and Stilbite are the main precipitates.

pH and silicon concentration evolutions can also be predicted during debris dissolution, cf. Figures 2 and 3. A slight pH increase can be observed. At the beginning, the increase is more marked because all the concrete is dissolved ; after, only glass fiber dissolution happens. This pH increase is consistent with literature data about glass fiber corrosion in alkaline media (Carmona and al., 2005).

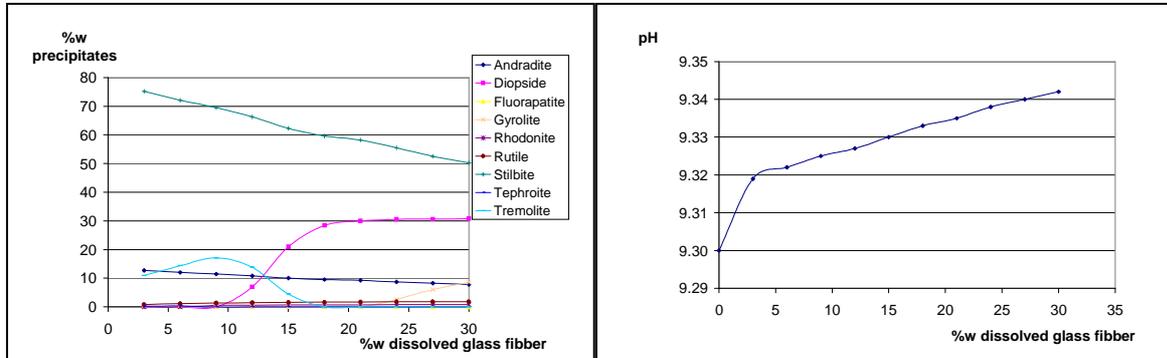


Figure 1. Percentage of precipitates formed versus dissolved glass fiber.

Figure 2. pH versus dissolved glass fiber.

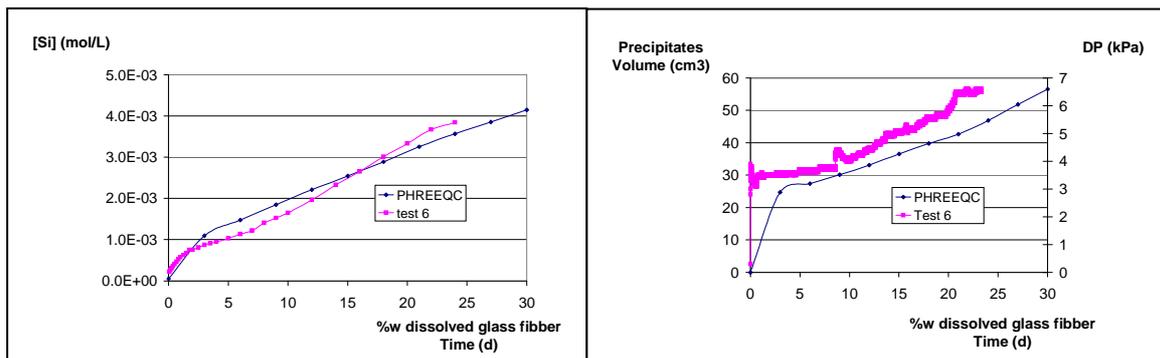


Figure 3. Silicon concentration versus dissolved glass fiber.

Figure 4. Precipitates volume and head loss versus dissolved glass fiber.

Figure 3 represents the comparison between silicon in solution, the main constituting element of glass fiber, measured during ELISA test 6, and the calculated Si concentration value. The agreement is quite good, that could mean that the assumption concerning the linear dissolution rate, 1%<sub>w</sub> per day, is grounded enough.

Figure 4 shows the volume of precipitates evolution as a function of the percentage of dissolved glass fiber, calculated with PHREEQC simulation ; the head loss measurements for ELISA test 6 are also reported. It can be shown that there is a correlation between the total volume of precipitates and the head loss measurement.

PHREEQC calculations were performed with and without taking into account paint dissolution. Results indicate that pH evolution is not altered by the supplementary presence of paint. In terms of precipitates, the Rutile precipitate (TiO<sub>2</sub>) is created but in low quantity. As seen in § 3.2, paint is mainly composed of titane (29%<sub>w</sub> of TiO<sub>2</sub>) but it contains very little Silicon, negligible in comparison with glass fiber and concrete content. As a consequence, paint does not significantly affect the total mass of precipitates.

To sum up, PHREEQC appears to be a suitable tool to simulate precipitate formation during the debris dissolution in sump. Next step is to assess the relative importance of each parameter onto the mass of precipitate formed.

## 4. Sensitivity study

The aim of this sensitivity study is to highlight the effect of different parameters on the mass precipitate formed. It is also useful to identify the favourable conditions which reduce the mass of precipitates formed, and therefore minimise the “chemical effects” on sump screen clogging.

In a first approximation, this sensitivity study is performed with all debris, except paint because its influence is limited due to its low corrosion. Anyway, its consideration in PHREEQC simulations using ELISA test conditions does not notably change results, as also evidenced experimentally.

The parameter variation range is gathered in Table 3 ; ELISA test conditions are indicated in bold.

Table 3 : Sensibility study conditions for 550 L of sodium-borate solution

Parameter	Value/Nature						
Temperature	30°C	45°C	<b>60°C</b>	75°C	90°C	140°C	170°C
pH	4.0		5.4		7.0		<b>9.3</b>
Mass of debris	Gf=167.2 g ; C+D=18.4 g		<b>Gf=836 g ; C+D=92 g</b>	Gf=4180 g ; C+D=460 g			
Nature of concrete	<b>ELISA</b>		Flamanville PWR		Gravelines PWR		
[Ca] in IRWST	0.01 ppm		<b>0.1 ppm</b>		1 ppm		

(Gf = glass fiber ; C = concrete ; D =dusts)

Influence of each parameter will be studied separately. The PHREEQC result is presented in terms of volume of precipitates formed corresponding to glass fiber dissolution up to 30%<sub>w</sub>. The reference case corresponds to the volume of precipitates obtained for French 900 PWR conditions and a break size of 28”.

### 4.1 Effect of temperature

PHREEQC calculations can be performed between 0°C and 300°C.

The temperature range (30°C-170°C), representative of those prevailing in the sump in case of a LOCA, is divided in seven temperature steps.

The minimal volume is obtained at 100°C, as shown in Figure 5.

Whatever the temperature is, Gyrolite is still present in not trifling quantity, with a maximum at 55°C. Gyrolite has a low density, resulting for an equivalent mass, to a more important volume. Luke (Luke, 2004) mentions the Gyrolite formation when concrete is submitted to temperature lower than 330°C, that is our case. Jauberthié (Jauberthié and al., 1996) has shown that formation of Gyrolite crystals happens after previous formation of Gyrolite gel, however this gel appears only at temperature higher than 120°C.

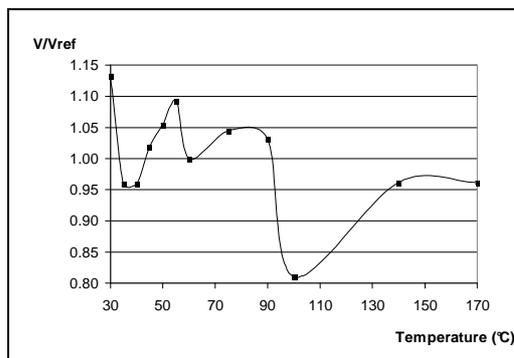


Figure 5. Percentage of precipitates formed versus temperature.

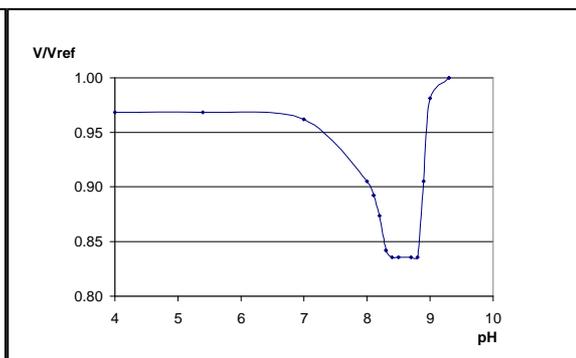


Figure 6. Percentage of precipitates formed versus pH.

At 30°C, formation of SiO<sub>2</sub>(am), which has also a very low density, also leads to a high volume of precipitates.

At 35°C, volume of precipitates presents a minimum when analysing the composition of precipitates obtained at 30°C, 35°C and 40°C, the amount of Gyrolite and/or SiO<sub>2</sub>(am) is minimal at 35°C, whereas quantity of Stilbite and Tremolite remains constant ; then the volume of precipitates is minimal. According to results from experiments performed in VUEZ, it has been experimentally observed that near this temperature, the head loss increase was the most important. It can be assumed that this evolution is not only dependent on the volume of precipitates but also maybe on the presence of gel.

## 4.2 Impact of pH

For « base » case, sump is alkaline. ELISA tests were performed at pH 9.3 ; this pH value is reached by addition of sodium hydroxide. Acid sump has been studied because it can correspond to LOCA accident for which CSS does not operate (no injection of sodium hydroxide).

Influence of pH on the volume of precipitates was investigated. It can be observed that minima values are obtained for pH around 8.5. This is due to the fact that for 8.4 ≤ pH ≤ 8.8 there is no Gyrolite formed, promoting a high volume of precipitates. Besides for pH 8.9 ≤ pH ≤ 8.3 there is no SiO<sub>2</sub>(am). Stilbite quantity remains about constant for all pHs.

Let's recall that debris dissolution process has been considered unaltered by pH variation to perform such parametric study.

For 30%<sub>w</sub> of glass fibber dissolved at pH =9.3, the whole volume of precipitates is increased of 20% with respect to pH 8.7.

## 4.3 Influence of the concrete composition

Two main types of concrete were used to build nuclear power plant ; the siliceous one, that contains more than 50% of silica, and the silica-limestone, rich in Ca.

The concrete of Flamanville PWR is of siliceous type, while the concrete of Gravelines PWR is of silica-limestone kind. Their molar weight are identical, M<sub>w</sub>= 18.04 g.mol<sup>-1</sup>.

Prototypical chemical composition for these two types of concrete are :

- concrete of Flamanville : Si<sub>0.2418</sub>Al<sub>0.0079</sub>Ca<sub>0.0349</sub>C<sub>0.0016</sub>H<sub>0.1202</sub>O<sub>0.5936</sub> ;
- concrete of Gravelines : Si<sub>0.0749</sub>Al<sub>0.0085</sub>Ca<sub>0.1344</sub>C<sub>0.1017</sub>H<sub>0.1201</sub>O<sub>0.5604</sub>.

In Figure 7, it can be seen that volume of precipitates is higher for siliceous concrete with respect to silica-limestone concrete.

At the start of the debris dissolution (≤ 3%<sub>w</sub>), no Gyrolite is formed whatever the concrete involved. The highest volume of Stilbite is obtained for ELISA concrete type. For Gravelines, a large volume of Calcite is predicted, this precipitate has also a low density. These two points explain why the total volume of precipitates is higher for these two types of concrete than for Flamanville concrete.

At the end of the dissolution (30%<sub>w</sub>), volume of Gyrolite in Flamanville concrete is equivalent to the Diopside volume for ELISA and Gravelines concretes. In addition, Stilbite volume for ELISA concrete is twice higher than that generated from Flamanville and Gravelines concretes. Calcite volume in Gravelines concrete, not present for Flamanville and ELISA concretes, is the same than the Stilbite one.

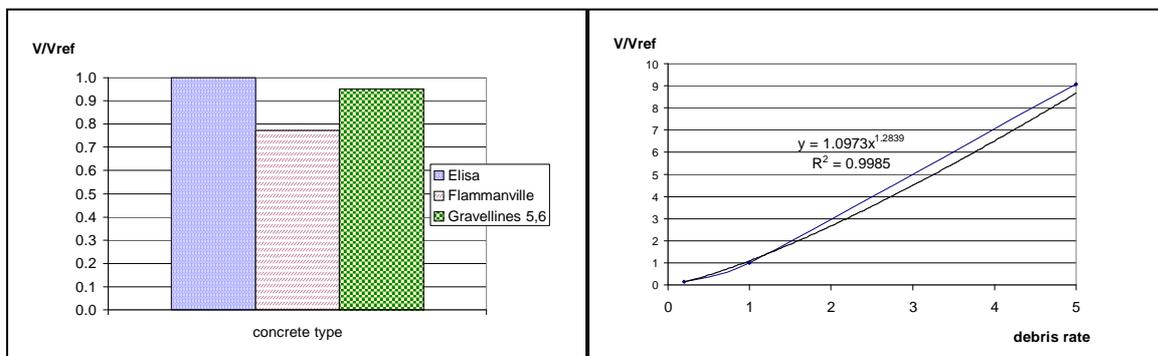


Figure 7. Percentage of precipitates formed versus nature of concrete.

Figure 8. Percentage of precipitates formed versus debris rate.

As a consequence, total volumes of precipitates in Gravelines and ELISA concretes are quite equivalent and anyway higher than the Flamanville one.

To sum up, concrete of siliceous type is less critical with regards to the sump clogging issue because a weaker volume of precipitates is formed.

#### 4.4 Effect of debris mass

For this study, we have chosen to work at lower and upper limits to better outline the trends. The low mass of debris corresponds to 1/5<sup>th</sup> of the standard value of the ELISA tests and, the highest mass to five times the ELISA value.

Figure 8 shows that for the upper mass, as expected, the mass, and as a consequence the volume of precipitates, are much higher.

For the lower mass, no pH variation is predicted and the volume of precipitate represents about 14% of that obtained in ELISA test simulations, while for the upper debris value, the precipitate volume is multiplied by about 8.5. A correlation can be extrapolated from these results as shown in Figure 8 :

$$\frac{V}{V_{ref}} = r^{1.28} \quad R^2=0.9985 \quad (1)$$

With :  $V$  : precipitates volume (m<sup>3</sup>) ;

$V_{ref}$  : precipitates volume in ELISA test conditions (m<sup>3</sup>) ;

$r$  : debris rate.

Mass of debris impacts the nature of the main precipitates. For low debris masses, Mesolite, Saponite-Na and after Tremolite are precipitated, and at the end of the debris dissolution, Stilbite. On the opposite, for higher debris masses, major components are Stilbite and Gyrolite and, at the end of dissolution , Tremolite and Clinoptilolite-hy-Na appear.

As expected, the larger the primary break is, the higher the mass of debris generated and the volume of precipitates will be.

## 5. Conclusions and prospects

The first objective of this parametric study was to investigate the impact of corrosion of the various kind of debris (glass fiber, concrete and paint) onto formation of precipitates. The resulting simulations performed with PHREEQC software are correlated with the experimental data coming from the « analytical chemical » and « head loss » experimental programs supported by IRSN ([Mattei, to issue](#)), in quantitative and qualitative terms. The second objective was to perform a sensitivity study to provide information with the relevance of each physical parameter on precipitate formation.

Trends on variation of the total precipitate volume as a function of boundary conditions can be drawn as follows :

- pH is a key parameter ; it has a strong influence on mass and volume of precipitates formed. In alkaline conditions, in the pH range 8.4-8.8, the amount of precipitates is much lower than for pH 9.3 ;
- temperature is an influential factor on formation of precipitates too. Temperature lower than 30°C or in the range 50°C-55°C promotes the generation of an important precipitate volume ;
- mass and volume of precipitates formed does not vary linearly with the immersed mass of debris ;
- paint seems to have a limited effect on precipitates formation, mainly due to its weak corrosion ;
- nature of concrete, more or less rich in silica, affects the total precipitate volume. A siliceous concrete is less penalizing for strainer clogging.

To sum up, the most important factor is the mass of debris generated, resulting from the jet steam impact onto local structures around the break.

A restriction to this sensitivity study is that the « kinetic of debris dissolution » was simply modelled by a constant dissolution rate of 1%<sub>w</sub> per day but it can be strongly affected by parameters like temperature or pH. Influence of the boundary conditions on effect of dissolution rate remains to be experimentally quantified.

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## Chemical formula of precipitates

- Calcite :  $\text{CaCO}_3$  ;
- Clinoptilolite-hy-Na :  $\text{Ca}_{1.7335}\text{Al}_{3.45}\text{Fe}_{0.017}\text{Si}_{14.533}\text{O}_{36} : 11.645\text{H}_2\text{O}$  ;
- Diopside :  $\text{CaMgSi}_2\text{O}_6$  ;
- Gyrolite :  $\text{Ca}_2\text{Si}_3\text{O}_7(\text{OH})_2 : 1.5\text{H}_2\text{O}$  ;
- Mesolite :  $\text{Na}_{0.676}\text{Ca}_{0.657}\text{Al}_{1.99}\text{Si}_{3.01}\text{O}_{10} : 2.647\text{H}_2\text{O}$  ;
- Saponite-Na :  $\text{Na}_{0.33}\text{Mg}_3\text{Al}_{0.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$  ;
- Stilbite :  $\text{Ca}_{1.019}\text{Na}_{0.136}\text{K}_{0.006}\text{Al}_{2.18}\text{Si}_{6.82}\text{O}_{18} : 7.33\text{H}_2\text{O}$  ;
- Tremolite :  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  ;
- Trephroite :  $\text{Mn}_2\text{SiO}_4$ .