GEO-VISUALIZATION OF AGGREGATE FOR AAR PREDICTION AND ITS IMPORTANCE FOR RISK MANAGEMENT

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Abstract

The paper summarizes the authors' findings regarding alkali-silica reactions in constructions made from OPC concretes. It gives a lot of examples confirming that AAR play a role at alkali-silica gels' formation in specific cases. Due to low alkali content in Portland clinker of commercially distributed cements, this process does not usually occur. In the paper, results of micropetrographic and chemical analyses and EDX analyses of volcanic aggregates are given. Along with them, chemical analyses of binder separated parts (of so called SiO₂ reactive forms) and influence of carbonate aggregates are discussed. Influence of carbonate aggregates is considered as one of ASR and ACR causes. Subsequently, sulphate attack and zeolitization of OPC concretes accompanying ASR are discussed. Thus, geovisualization of aggregate micropetrographic composition together with examination of OPC microchemical composition may considerably contribute to decrease of potential ASR, sulphate attack and zeolitization in concrete constructions. These findings represent important information for risk management.

Keywords: Portland cement concrete, alkali-silica reaction, sulphate attack, hydrocarbonates, volcanic aggregates.

1 INTRODUCTION

Aggregates containing certain constituents can react with alkali hydroxides in concrete. The reactivity is potentially harmful only when it produces significant expansion. This alkali-aggregate reactivity (AAR) consists of two forms of alkali-silica reaction (ASR) and alkali-carbonate reaction (ACR, sometimes called alkali-carbonate rock reaction, or ACR). ASR is of more concern than ACR because the occurrence of aggregates containing reactive silica minerals is more common. Alkali-reactive carbonate aggregates have a specific composition that is not very common.

The alkali-silica reaction is not fully understood, but the following characteristics are accepted by most researchers:

- a) The reaction occurs between amorphous or cryptocrystalline forms of silica in the rock and hydroxide ions in the cement paste porous solutions.
- b) The concentration of hydroxide ions in solution is largely determined by the amount of alkali metal (Na and K) in the cement.
- c) The product of the reaction is a gel which may imbibe water and swell [1].

In the presence of free moisture, the gel will expand and cause cracking and differential movements in structures, as well as other deleterious effects such as reductions in freeze-thaw durability and in strengths properties of concrete [2].

The primary role of sodium and potassium is to increase the pH so that the Si-O-Si bonds in the silica are attacked by OH- ions. It is assumed that gels with very high alkali metal content are fairly fluid and can move through the paste causing little damage. The incorporation of calcium into the gel is often considered to be a secondary reaction, taking place sometime after the initial formation of the gel, and it has been claimed that calcium-containing gels are not expansive [1].

Experimental investigations of the reactions between silica, alkali hydroxide solution, and calcium hydroxide show that alkali–silicate–hydrate gel (A-S-H) comparable to that formed by the alkali–silica reaction (ASR) in concrete does not form when portlandite or the Ca-rich, Si-poor C-S-H of ordinary Portland cement (OPC) paste is available to react with the silica.

These conclusions indicate that the ASR gel of concrete forms only in chemical environments in which the pore solution is much lower in Ca and higher in Si than bulk pore solution of OPC (ordinary Portland cement) paste. These results highlight the similarity between ASR and the pozzolanic reaction. [3]

Another deleterious process which appears together with ASR is sulphate attack. The effect of the alkaline ions on CaO-Al₂O₃-CaSO₄-H₂O system is not perfectly known due to its complexity.

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However, it has been demonstrated that when alkalis are present in the dissolution, the concentration of sulphates and carbonates in the invariant points are higher; that is to say, the stabilization of the solid phases need higher sulphate and carbonate concentrations in the dissolution [4].

The effect of the alkali-aggregate reaction is also important in the thaumasite formation. Gels produced by the alkali-aggregate reaction show important chemical variations. Within them, ettringite and thaumasite are occasionally found. This may suggest that thaumasite is replacing the ASR gel [5] and [6].

Thaumasite has been found, usually co-existing with secondary ettringite, within concretes damaged as a result of the alkali-silica reaction (ASR) [7].

Another example of thaumasite associated with ASR-affected concrete was found in the Les Cedras dam in Canada [8]. In this case thaumasite precipitation occurred along the interface between dolomite aggregate and cement paste.

The occurrence of thaumasite has also been found in concretes suffering from delayed ettringite formation (DEF). This discovery was made by Sylla in Germany [9], whilst examining heat-treated precast concrete components such as steps, cooling tower supports, floor slabs, concrete piles and prestressed beams, which had cracked during service. Microanalysis of acicular crystals found in cracks and around aggregate particles revealed them to comprise either ettringite, thaumasite or mixed crystals of both. It was concluded that precipitation of such crystals had led to expansion within microcracks as well as to loss of strength of concrete due to decomposition of the strength-forming hydration products.

A low rate of sulphate attack is necessary in order to produce thaumasite. The detection of syngenite has raised the problem of the role of the alkalis. Their presence contributes to the change of the pH. They, moreover, remove $(SO_4)^{2-}$ from the solution in order to create syngenite, which is less soluble than gypsum [4], [10].

Field experience shows that ASR occur in combination with DEF (delayed ettringite formation) – type of sulphate attack. [11].

It is generally thought that this is because the formation of ettringite is a precursor to that of thaumasite. They both have very similar structures and the topochemical interchange of [Si] for [Al] and $[CO_3^{2^-} + SO_4^{2^-}]$ for $[SO_4^{2^-} + H_2O]$ results in a solid solution series between the two minerals.

Thaumasite was first discovered as a product of sulphate attack in concretes in the USA in 1965 [12].

The catalytic influence of ettringite on the formation of thaumasite has been confirmed by Lachaud [13]. Gaze and Crammond [14] have already shown that thaumasite forms at pH values from 13 down to 10.5.

García del Amo and Pérez [5] proposed evaluating of reactivity of quartz using quartz reactivity index (QRI). These values were obtained by multiplying the percentage of quartz in the aggregate by its specific surface area. These results have been related to alkali reactivity as measured by an accelerated mortar bar test. The authors demonstrated that the reduction of grain size in quartz (here, produced by the metamorphic processes) greatly enhances alkali reactivity by increasing the surface area of quartz grains available for the reaction.

Using a low-alkali cement with less than 0.6 Na₂Oe or limiting the concrete alkali content constitutes the most popular way to ensure that the alkali concentration is low enough in the concrete pore fluid to minimize ASR in the presence of potentially reactive aggregates [15].

Some aggregates may also, with time, supply significant amounts of alkalis' to the concrete pore solution. This could explain why many concrete structures are affected by ASR, although built with low-alkali cements (<0.6 Na₂O_e) as in the case of many dams [16]. Authors have not come across this phenomenon in the Slovak Republic.

2 MATERIALS AND METHODS

2.1 Field methods

Many of drill cores were macroscopically examined immediately after drilling. Later, a set of cores (7 samples) was selected for following laboratory analytical studies.

2.2 Laboratory methods

Macroscopically observable characteristics as colour, structure, macro-porosity, secondary minerals etc. were described using stereomicroscope. After that the samples were disintegrated for following laboratory processing. Polished sections were prepared from representative rock samples (both aggregate particles and rocks from original natural locality). These samples were used for assessment of relations between minerals associated in studied rock samples. Further, microstructure, mineral composition and crystallization sequence were studied. Microscopic analyses were carried out using polarizing microscope OLYMPUS BX 51. Photographic documentation of thin sections was carried out by Nikon Coolpix camera. Polished sections were coated by carbon after execution of basic microscopic description and used for study of microchemical composition of selected mineral groups. Chemical composition was determined in the Microchemical laboratory of the Institute of Geological Sciences, Masaryk University in Brno under the electron microscope Cameca SX 100.

Optical properties, of both aggregates and matrix, were studied using Olympus BX 51 microscope. EDX analyses have been executed on the Cameca SX 100, 15kV, and 10nA (for zeolites it was 4 kV and 40 nA). Lower limit of detection is typically around 0.1wt% for oxide.

X-ray analyses and wet chemical analyses were carried out for exact identification of individual mineral phases and aggregates' classification.

3 GEOLOGICAL SITUATION

Examined concrete samples come from lining of a railway tunnel in Banská Štiavnica. The tunnel was driven in the middle of 20. century and is 1187 m long. It is made of 149 belts, mostly 8m long each. Scuncheon was built of rocks or of rocks and concrete. The concrete aggregate consist of andesite and rhyolite rocks. The aggregate was delivered from Kysibla (rhyolite) and Babiná, Georgi štolňa (andesite) sites. Cement came from Lietavská Lúčka cement works. Reverse side of the vault is almost completely isolated. The isolation is mostly represented by asphalt slabs (1002m) or metal plates (112m). The isolation material and locally also the rock lining is – to various degree – deteriorated.

The tunnel is built in a massif of Tertiary volcanic rocks (first of all andesite tuffs intercalated by thick andesite zones (Figure 1). The rocks are eroded to various degree – from untouched to completely eroded. The degree of erosion decreases towards the interior parts of the massif. The main deterioration factor (first of all of concrete) is chemical composition of water.

The macroscopic appearance of examined concretes with andesite and rhyolite aggregates can be seen on drill cores (Figure 2).

4 RESULTS

4.1 Petrographical situation

Aggregate of examined altered concretes is mixed. Together with below listed volcanic rocks, limestones, dolomitic limestones up to dolomites occurred in all studied samples. The fragments of carbonate rocks reach max. 2 cm. No microfossils were identified there. The carbonate rocks belong to medium up to coarse grained sparites.

Regarding examined aggregates, tuffs, tuffites and partly devitrified glass represent the main potential risk for ASR and ACR.

Andesites

Porphyritic andesites, propylized andesites and andesite tuffs can be macroscopically recognised among the andesite aggregates.

Microscopically, it can be seen that the most of andesite aggregates have a porphyritic microstructure. The phenocrysts are represented by plagioclases, amphiboles, biotite, less common is pyroxene.

Amphiboles form up to 5mm long columnar crystals. They are usually lined with opaque lining formed by magnetite, less often by ilmenite. The amphibole individuals are dark brown and distinctly pleochroic.

Biotite is rare. It forms deep red-brown thick tabular crystals with distinct pleochroism (X – light brown, ZY- deep red-brown). Biotite often has an opaque lining. Ilmenite was not identified there.

In comparison with the above listed minerals, light brown pyroxenes are much rarer. They most often reach 0.5-2mm.

In propylitized clasts, these mafic minerals are completely pseudomorphosed by chlorite, epidote, less frequently by prehnite. In pyroxene alteration products, light green, hairy actinolite crystals are present.

The largest are plagioclase phenocrysts reach 5–10mm. They are tabular, distinctly polysynthetically twinned, often zonal or complicated intergrowths and oscillation zones are developed there. Plagioclases are usually altered. Calcite, epidote and sericite occur among the alteration– products. Matrix contains small lathlike plagioclases surrounded by glass. Amphiboles, biotite and pyroxenes are not parts of matrix. Matrix glass phase was always devitrified (chlorite, calcite, epidote, opaque and minerals occur there).

Rhyolites

In rhyolite aggregates, porphyritic, porous and kaolinitised rhyolites and rhyolite tuffs can be macroscopically distinguished.

Brown-red rhyolites have a fine porphyritic structure, locally distinctly porous. Phenocrysts of sanidine, seldom by magmatically corroded quartz and relatively smaller plagioclases (oligoclase-andesine) are present there. The phenocrysts are surrounded by weak birefringent mass that is often pigmented by hematite. Some rhyolite fragments have very well developed fluidal microstructure. The size of the phenocrysts reaches 1–5 mm. Biotite is the only dark mineral in rhyolites. Alkali feldspars and quartz are very common components of matrix, but phenocrysts are very rare. Higher contents of dark minerals (biotite, amphibole and seldom pyroxene) are characteristic for dacites. The dark minerals are instable. Chloritised biotites and amphiboles are common there.

Rhyolite up to dacite tuffs are formed by lithoclasts, devitrified glass, clay minerals, carbonates and fragments of strongly altered minerals.

Portland clinker

According to entries of documentary records, the concrete mix was prepared from Portland clinker. In spite of the fact that the concrete is very deteriorated, we are still able to identify relics of unhydrated clinker minerals. Especially brownmillerite is very distinct. The hydration principal if summarized below.

It is assumed that each component of PC hydrates independently on the others. This is not completely true because interactions among the hydrating component will affect the mixture.

The hydration reactions of the two calcium silicates, which make up the largest percent of Portland cement, are similar. The basic products are: 1) calcium silicate hydrate, poorly crystalline material of extremely small particle size and 2) calcium hydroxide, a crystalline material. The reactions can be evaluated by the rate of heat generation.

The rate of hydration follows the sequence: $C_3A > C_3S > C_4AF > C_2S$.

4.2 Chemical composition

Chemical composition of aggregates

Fragments of aggregates were separated from the concrete so as individual rock types were collected. The separated rocks were analysed using wet-silicate analysis. The silicate analyses results (Table 1) were recalculated using GCDkit software for standard mineral norms. The standard quartz content in rhyolites, dacites and their tuffs reaches 48-14% (Table 1). The highest content of standard quartz was found in rhyolite tuff. There are high Al₂O₃ contents in the andesite and rhyolite tuffs (among the normative minerals of andesite tuffs, normative corundum contents exceed 20 %). Standard calcite occurs in some tuffs.

Comments: 1,2,3 andesite; 4,5,6 andesite tuff; 7,8 rhyolite; 9 rhyolite tuff; 10,11 dacite; 12 dacite tuff.

Chemical composition of alteration products

Alteration products present in deteriorated concretes consist of ASR and ACR gels, sulphates, zeolites and tobermorite. Along with microchemical examination, migration of elements was studied. This migration accompanies sulphate attack and zeolitization of concrete. The change of elemental distribution in ACR gels (playing an important role in concretes with rhyolite aggregate) confirms assumption of hydrocarbonate formation (Figure 3, 4A, 4B and 4C).

Chemical composition of gels

Gels identified in the examined concretes have various chemical compositions (Table 2). Considering a type of aggregates, a certain rules of their composition are observable there. Gels identified in concretes with rhyolite aggregates have a higher SiO₂ content, various contents of CaO and FeO and a lower Al₂O₃ content than in gels with andesite aggregates. K₂O and MgO contents display no regularities. Na₂O content is insignificant. Remaining identified oxides are present in trace concentrations. In Figure 2 and 3, zonality of gels, their recrystallization to zeolites, hydrocarbonates and alkali feldspars are well distinct. The results of their chemical analyses probably correspond to gels formed by combination of ACR and ASR.

Chemical composition of zeolites

In concretes with rhyolite aggregates, new-formed zeolites were identified in the porous system along with gels and sulphates (Figure 3A, 3C and 5). These zeolites chemically correspond to stellerite (CaAl₂Si₇O₁₈·7(H₂O)) – see Table 6.

Figure 4A shows stellerite crystals in a binder pore lined with zonal Ca, Mg, Al and Si gels. It is obvious that the gels' margins are chemically close to hydrocarbonates. In the upper part of Figure 4B, new–formed alkali feldspars (Na>K albite) can be identified there. Migration of K, Na, Al and a part of Si to new–formed alkali feldspars gradually decreases their content in gel. In the middle and in the bottom left corner of the image (Figure 4B) a distinct elemental differentiation may be observed. In the bottom left corner, the gel is enriched with K, Al and Si. In the image middle part in the gel solid solution, these elements' contents are reduced. Mg content is higher and Al content is medium there. Content of Ca and Fe is significantly lower and adequate to Mg and Al contents. The gels' exterior part is usually optically isotropic. If we accept the assumption that (except of ASR) also ACR gels occur, then formation of their hydrocarbonates may be expected there. Microcrystalline and nanocrystalline character of the linings' exterior part, elemental distributions and their zonality would correspond to manasseite, sjögrenite and sergeevite[†]. These hydrocarbonates gradually develop from ACR gels and they are optically identifiable (Figure 5). In the bottom right hand corner of Figure 4B, there is ettringite (Ca, Al, S). Cl distribution documents chlorides' migration through porous solutions and their catalytic effect in ASR gels' sulphate attack.

In Figure 4C, the elemental distribution documents more significant stage of "zeolitization", alkali feldspathization and recrystallization of ASR and ACR gels. Al, Na and K, along with Si adequate portion gradually form in alkali feldspars' structure. Manasseite is replaced by sjögrenite and sergeevite (Figure 4C). In the gels, zonality is conditioned by distribution (migration ability) of Ca, Al, Mg, Fe and Si. In the outer rim, the lining is enriched by Ca and Al. Under this part of the lining, there is a zone with a relative high concentration of Mg and Fe. Towards the new–formed alkali gels, the concentration of Mg and Fe decreases and Ca content slightly increases. The Ca content also increases toward the zeolite individuals. Mg and Fe concentrate in the linings' central parts. On the contrary, there is a zone slightly enriched by Ca in the contact with new-formed alkali feldspars. There is always a relative high content of Cl in the zeolite–gel contact. Again, chlorides act as catalysers here.

Chemical composition of tobermorite

In concretes with mixed rhyolite–carbonate aggregate, the gels are gradually replaced by tobermorite[‡] crystal clusters (Figure 5). The most of analysed tobermorite individuals displayed distinct predominance of Mg over Ca. It probably is Mg–tobermorite. The results of chemical analyses are given in Table 4.

4.3 Products of sulphate attack

Sulphates were identified in the pores of concretes with rhyolite and andesite aggregates. These were represented by ettringite–thaumasite up to ettringite solid solutions in samples with andesite aggregate (Tables 5 and 6) and ettringite in samples with both andesite and rhyolite aggregate. Chemical composition of ettringite individuals are recalculated for formula – see Table 6.

Brown calcite forms (Figures 6 and 7) and white ettringite-thaumasite needles (Figure 8) form sustained water infiltration on the surface of concrete. The corrosion and minerals' formation proceeds also in the front side of the examined concretes. The railway tunnel concrete contains cavities up to a few centimetres large.

5 DISCUSSION

Stellerite formation in cavities of concrete with rhyolite aggregate is a typical example of an anthropogenic influence. Stellerite does not occur in the volcanic complex of the tunnel's surroundings [18]. Conditions of its formation and stability were studied with the aspect of AAR (ASR and ACR), sulphate attack and carbonation.

The results proved that the alteration of the examined concretes is related to aggregate type. Volcanic rocs were along with limestones and dolomitic limestones added to OPC paste. In the volcanic aggregate, also andesite, rhyolite and dacite tuffs and tuffites and devitrified glass were present there. Alkali conditions

⁺ Manasseite Mg₆Al₂(CO₃)(OH)₁₆.4H₂O; sjögrenite Mg₆Fe₂(CO₃)(OH)₁₄.5H₂O and sergeevite Ca₂Mg₁₁(CO₃)₉(HCO₃)₄.6H₂O

[‡] Tobermorite Ca₅Si₆O₁₆(OH)₂.4H₂O

^{*} Water % correspond to theoretical value derived from the sum of the other oxides

represented a good predisposition for expansive gels' formation. The presence of limestones and dolomitic limestones enabled both types of AAR (ASR and ACR). Formation of expansive gels resulted in microcracks' formation in the beginning stage. A low water supply or a complete desiccation leads to a formation of contraction microcracks. The microcracks enable transportation of mineralised solutions and crystallization of salts in the voids.

Alkali-carbonate reactions (ACR) were observed in presence of dolomitic rocks aggregates. Dedolomitization, the decomposition of dolomite, and subsequent crystallization of brucite may cause considerable expansion. The deterioration caused by ACR is similar to that caused by ASR. However, ACR is relatively rare because aggregates susceptible to this phenomenon are less common and are usually instable for use in concrete for other reasons. Aggregates susceptible to ACR tend to have a characteristic microstructure that can be identified petrographically.

Alkali-carbonate reactivity consists of several different reactions which may take place between carbonate rock aggregate particles and the cement paste of Portland cement concrete. The composition of the carbonate rock allowed determines which type of reaction occurs. For example, non-dolomitic carbonate aggregate particles may develop reaction rims which dissolve more rapidly in dilute acid than the interior of the particle. Similarly, impure dolomitic limestone (that is, limestone composed of large dolomite crystals in a fine-grained calcite and clay matrix) aggregate particles may develop silica-enriched rims. Although in both situations a reaction clearly has taken place between aggregate particles and cement paste, neither reaction affects the concrete deleteriously. The only form of ACR known to be harmful to concrete is the "dedolomitization" reaction which may take place between argillaceous (clay-rich) dolomitic limestone aggregate particles and the high pH of the pore fluids in cement paste.

In the first phase of dedolomitization, pore solutions with a high pH break down dolomite to form calcite, brucite and carbonate ions. The net reaction will proceed until either dolomite or Portlandite is exhausted:

$$CaM_g(CO_3)_2 + Ca(OH)_2 \Longrightarrow 2CaCO_3 + M_g(OH)_2 \tag{1}$$

During dedolomitization, dolomite and lime are replaced by brucite and calcite, minerals with a slightly greater volume than the reactants. This reaction has little effect on the total volume of the concrete. However, considerable expansion occurs locally, at the rims and in the zones surrounding reactive aggregate particles, where calcite and brucite are deposited. Because of this, ACR often leads to a loss of bond between aggregate particles and cement paste. Typically, microcracks originate at the reactive rims, radiate into the aggregate particles and propagate outward well into the paste. Chemical depletion may also produce voids in the reacted dolomite aggregate particles. Hydrocarbonates of mannasite type (Mg₆Al₂(CO₃)(OH)₁₆.4H₂O), sjoregenite (Mg₆Fe₂(CO₃)(OH)₁₄.5H₂O) and sergeevite (Ca₂Mg₁₁(CO₃)₉(HCO₃)₄.6H₂O) must be considered typical mineral phases forming from ACR gels (or rather cobined ACR+ASR gels). Tobermorite (Ca₅Si₆O₁₆(OH)₂.4H₂O) with significant Mg content, which was also identified, probably forms from CSH gels. High Mg content documents role of brucite saturated solutions during its formation.

The above listed hydrocarbonates have not been identified in concrete so far. They occur in altered carbonate and volcanic rocks [http://webmineral.com].

Stellerite was identified in pores of concrete with rhyolite aggregate. Stellerite always occurs in a close distance from hydrocarbonates' zones. Its formation is probably related to reactive suspended water enabling elements' migration and reacts with ACR and ASR gels. Stellerite is known from metabasalt tuffs and it is not present in mineral parageneses of the Slovak Neovolcanites.

Ettringite-thaumasite solid solutions are the most frequent sulphate attack products here. "Pure" ettringite and thaumasite were not found. Their existence and stability at the presence of $(CO_3)^2$ - was studied by Barnett, Adam and Jackson [19]. Kollman and Strübel [20], for instance, reported that if the silicate in the CSH gel dissolves – or the Si⁴⁺ is incorporated or combined – in the presence of carbonate and at temperatures from 1 to 5 °C, ettringite "turns into" thaumasite almost completely after 40 days, during a process accompanied by expansion. Pajares, Martínez-Ramírez and Blanco-Varela [21] carried on experimental examination of conditions of ettringite decomposition at the presence of carbonate ions. Ettringite was put in the contact with three types of saturated solutions: (a) CaCO₃ and silica gel saturated solution; (b) MgCO₃ and silica gel saturated solution and (c) C–S–H gel plus portlandite and CaCO₃ saturated solutions, calcite, magnesium carbonates, silica gel etc., were put in permeable bags hanging in the water. The temperature of the experiment was 4 ± 2 °C. Other authors [13] claim that ettringite exerts a catalytic effect on thaumasite formation. However, our analyses did not prove it. The experiment when lime and $Al_2(SO_4)_3 \cdot 17H_2O$, pure grade were mixed in a sucrose solution in order to synthesise ettringite showed that ettringite evolution in the studied solutions proceeds in a different way. In the presence of CaCO₃ and silica gel, ettringite decomposition starts at 130 days. When MgCO₃ is present instead of CaCO₃, ettringite, decomposition starts at 90 days. The ettringite decomposition was not observed in geochemically open systems, even though the presence of all the other phases (taking part in the experiment) was proved. Alunite is a common mineral of the Slovak Neovolcanites' parageneses.

5 CONCLUSIONS

The results confirmed a close relation between AAR, sulphate attack, and saturated solutions of portlandite, brucite, CaCO₃ and CSH gels. Trace amounts of Cl⁻ (2NaCl +Ca(OH) \leftrightarrow Ca(Cl)₂ +2NaOH) confirm its catalytic effect. It takes part in both, sulphate attack and zeolitization of ASR and ACR gels. Influence of ACR and ASR gels on formation of expansion and contraction ruptures was perceptible in all examined concretes. Reactions of gels with weak sulphuric and hydrocarbon acids, hydroxides of Al, Mg and Ca at the presence of halite (possibly other catalyzes) under low temperatures (max.15°C) acting for a long period lead to thaumasite and ettringite formation. We assume that AAR leading to ASR and ACR gels' formation along with high Ca and Mg contents in migrating water might form conditions for the formation of zonally arranged hydrocarbonates – manasseite, sjögrenite and sergeevite. On the surface of concrete, the surplus Ca(OH)₂ reacts with atmospheric CO₂ and SO₃ forming calcite and ettringite.

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	1	2	3	4	5	6	7	8	9	10	11	12
SiO ₂	62.2	63.2	59.8	48.9	51.9	50.2	72.2	75.8	70.1	70	71.8	72.9
TiO2	0.6	0.1	0.1	0.9	1	0.1	0.2	0.1	0.2	0.3	0.1	0.1
$\mathrm{Al}_2\mathrm{O}_3$	15.6	13.1	14.2	17.3	21.9	23.1	13.1	11.3	9.7	14.3	16.1	14.3
Fe ₂ O ₃	4.9	2.9	2.6	2.9	6.0	7.3	1.6	0.9	0.6	0.5	0.9	0.6
FeO	0.1	1.2	2.1	1.5	1.9	1.3	1.0	0.1	0.5	3.1	0.5	0.3
MnO	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.0	0.0	0.1	0.0
MgO	2.2	2.9	4.2	2.7	2.3	0.2	0.2	0.1	0.2	0.3	0.1	0.1
CaO	4.7	5.2	6.5	6.4	1.3	1.3	0.4	0.6	3.2	3.1	1.3	0.9
Na ₂ O	3.1	3.0	4.2	3.6	1.5	2.5	1.3	2.2	1.3	3.5	4.6	4.6
K_2O	2.9	2.2	2.4	2.1	1.4	1.2	8.8	7.3	3.2	2.9	3.7	5.4
Cl	0.1	0.2	0.3	0.4	0.5	0.5	0.0	0.2	0.2	0.0	0.1	0.2
SO ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0
$\rm CO_2$	0.0	0.0	0.0	2.1	0.0	0.3	0.0	0.0	2.4	0.0	0.0	0.0
P_2O_5	0.1	0.2	0.1	0.2	0.3	0.3	0.0	0.8	0.5	0.9	0.0	0.0
-H ₂ O	1.3	0.9	1.1	5.4	2.5	5.3	0.9	0.1	5.2	0.9	0.0	0.0
$+\mathrm{H_2O}$	1.2	1.1	0.9	5.2	7.2	6.3	0.2	0.0	2.3	0.0	0.1	0.4
sum	99.1	96.3	98.6	99.7	99.8	100	99.9	99.6	99.8	99.8	99.4	99.8

TABLE 1: Chemical composition of aggregates composed of volcanic rocks (andesite, rhyolite) and their tuffs.

aggregates			rhyolite		andesite						
sample	4/1	4/2	8/1	8/2	8/3	6/1	6/2	6/3	6/4		
	gel	gel	gel	gel	gel	gel	gel	gel	gel u ettringite		
SiO2	48.1	50.9	59.5	59.2	57.1	34.9	44.1	34.4	30.4		
CaO	13.6	8.8	4.4	4.5	5.5	11.0	5.1	9.0	18.0		
Al ₂ O ₃	6.8	6.1	16.0	15.8	15.2	19.9	23.2	19.4	5.2		
MgO	11.0	10.2	8.2	8.2	7.4	9.9	5.8	10.5	1.3		
FeO	5.8	11.4	1.4	1.5	1.3	8.3	6.3	8.9	7.8		
K ₂ O	0.3	0.4	0.7	1.1	0.9	1.2	5.3	1.0	1.1		
Na ₂ O	0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.1	0.8		
MnO	0.3	0.2	0.1	0.2	0.2	0.1	0.1	0.1	0.2		
P ₂ O ₅	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.3		
BaO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6		
SrO	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0		
SO3	0.1	0.0	0.0	0.0	0.0	0.4	0.1	0.2	1.5		
Cl	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.8		
Cr ₂ O ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2		
Total	85.9	88.1	90.4	90.5	87.6	85.9	90.0	83.7	68.7		

TABLE 3: Chemical composition of stellerite and formula recalculation. Analyzed by R. Čopjaková.

sample	4/1	4/2	8/1	8 / 2	8/3	Stt		4/1	4/2	8/1	8/2	8/3	Stellerite
SiO ₂	65.8	65.7	62.3	62.2	63.4	59.7	Si	7.3	7.2	7.0	7.1	7.1	7
Al ₂ O ₃	12.8	14.1	14.6	14.1	14.7	14.5	Al	1.7	1.8	1.9	1.9	1.9	2
FeO	0.0	0.1	0.0	0.0	0.0		Fe	0.0	0.0	0.0	0.0	0.0	
MgO	1.2	1.3	0.4	0.5	0.3		Mg	0.2	0.2	0.1	0.1	0.0	
CaO	4.6	5.3	6.9	6.4	6.9	7.9	Са	0.6	0.6	0.8	0.8	0.8	1
K ₂ O	0.8	0.6	1.0	0.9	1.2		K	0.1	0.1	0.1	0.1	0.2	
Na ₂ O	0.1	0.3	0.1	0.1	0.1		Na		0.1	0.0	0.0	0.0	
BaO	0.0	0.0	0.1	0.1	0.1		Ba			0.0	0.0	0.0	
SrO	0.0	0.0	0.2	0.1	0.2		Sr			0.0	0.0	0.0	
Total	85.3	87.6	85.7	84.7	86.8		0	18.0	18.0	18.0	18.0	18.0	18
+H ₂ O	14.7	12.4	14.3	15.3	13.2§	17.9	H ₂ O						7

TABLE 4: Chemical composition of tabular Mg - tobermorite individuals from concretes with rhyolite-andesite aggregate (sample

	/).												
	7/2	7/4	7/5	7/6	7/7	7/19							
SiO ₂	46.5	40.7	43.1	38.3	38.9	30.7							
$\mathrm{Al}_2\mathrm{O}_3$	9.6	11.1	8.6	8.2	9.8	5.6							
SO3	0.1	0.1	0.1	0.1	0.1	0.7							
FeO	0.6	1.1	0.0	0.2	0.3	1.6							
MnO	0.1	0.0	0.0	0.0	0.0	0.1							
MgO	24.4	24.5	27.4	24.6	26.0	3.7							
CaO	3.9	2.6	3.3	2.3	3.0	17.4							
Na ₂ O	0.0	0.0	0.1	0.0	0.0	0.0							
$K_{2}O$	0.2	0.6	0.1	0.2	0.2	0.1							
	Re	calcula	tion fo	or Ca+	Mg =5	5. Al+Si=6							
Si4+	5.2	4.6	4.7	4.7	4.5	5.3							
Al ³⁺	1.3	1.5	1.1	1.2	1.3	1.1							
S6+	0.0	0.0	0.0	0.0	0.0	0.1							
Fe ²⁺	0.1	0.1	0.0	0.0	0.0	0.2							
Mg^{2+}	4.1	4.1	4.5	4.5	4.5	1.0							
Ca ²⁺	0.5	0.3	0.4	0.3	0.4	3.2							
Na+	0.0	0.0	0.0	0.0	0.0	0.0							
K^+	0.0	0.1	0.0	0.0	0.0	0.0							
	11.1	10.7	10.7	10.7	10.8	11.0							
		Mg-t	oberm	orite		tobermorite							

TABLE 5: Chemical composition of ettringite-thaumasite solid solutions present in pores of deteriorated concretes with rhyolite aggregate (sample 7). Analyzed by R. Čopjaková.

-		455108	Sale (Sample	, /). milaiy20	a by R. Co	janova.							
sample	7-8	7-9	7-10	7-17	7-20	7-21	7-22	thaumasite					
SiO ₂	5.2	4.1	4.6	12.9	6.0	5.1	4.3	9.7					
Cl	0.7	0.8	0.8	0.3	0.7	0.7	0.5						
Al ₂ O ₃	5.8	5.7	5.2	4.4	6.5	7.7	8.1						
SO ₃	7.8	8.2	7.0	7.6	12.7	14.5	15.6	12.9					
CO ₂	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.1					
FeO	0.1	0.0	0.1	0.8	0.0	0.1	0.0						
MnO	0.0	0.0	0.0	0.1	0.0	0.0	0.0						
MgO	0.0	0.0	0.0	0.6	0.0	0.0	0.0						
CaO	19.1	18.7	17.3	14.9	23.9	27.4	27.8	27.0					
Na ₂ O	0.0	0.0	0.0	0.5	0.0	0.0	0.0						
K ₂ O	0.0	0.0	0.1	0.5	0.0	0.0	0.0						
P_2O_5	0.0	0.0	0.1	0.2	0.0	0.0	0.0						
Total	45.8	44.6	42.2	49.6	56.9	62.5	63.4						
Ca+Al+K+Na+Mg+Si+Fe=4; C+S=2 recalculated for 6 cathions													
Si ⁴⁺	0.6	0.5	0.6	1.4	0.5	0.4	0.4	1.0					
Cl^+	0.2	0.2	0.2	0.1	0.1	0.1	0.1						
Al ³⁺	0.8	0.8	0.8	0.6	0.8	0.8	0.9						
S ⁶⁺	0.7	0.8	0.7	0.7	1.0	1.0	1.1	1.0					
C4+	1.2	1.2	1.3	1.1	1.0	0.9	0.9	1.0					
Fe ²⁺	0.0	0.0	0.0	0.1	0.0	0.0	0.0						
Mg^{2+}	0.0	0.0	0.0	0.1	0.0	0.0	0.0						
Ca ²⁺	2.5	2.5	2.4	1.8	2.6	2.8	2.7	3.0					
Na+	0.0	0.0	0.0	0.1	0.0	0.0	0.0						
K^+	0.0	0.0	0.0	0.1	0.0	0.0	0.0						
sum cat	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0					

(sample / and 8) and andesite aggregate (sample 6). Analysed by K. Copjakova.																	
	7-11	7-12	7-13	7-14	7-23	7-24	7-25	7-26	7-27	8-4	8-5	8-6	6-1	6-2	9-3	6-4	Ett ¹
SiO ₂	1.1	1.1	0.9	2.3	1.3	1.0	0.8	0.3	0.4	0.2	0.3	0.4	0.4	0.2	0.1	0.3	
Cl	0.1	0.3	0.5	0.3	0.1	0.1	0.1	0.2	0.2	0.7	0.3	0.3	0.3	0.3	0.2	0.3	
Al ₂ O ₃	11.5	10.6	8.3	9.6	11.1	10.9	10.9	10.5	10.1	8.0	9.6	9.0	10.1	9.8	10.2	10.4	8.1
SO3	20.5	19.6	15.4	17.6	23.7	23.9	24.2	21.4	20.8	16.7	20.2	19.9	21.2	20.6	20.6	20.6	19.1
FeO	0.2	0.0	0.0	0.1	0.0	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
MgO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.0	
CaO	34.8	33.3	25.9	30.2	35.2	35.6	35.0	33.9	32.2	25.8	29.5	29.3	31.7	30.6	31.2	31.0	26.8
Na ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
K ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
P_2O_5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1	
Σ	68.3	64.8	50.9	60.2	71.5	71.6	71.1	66.4	63.8	51.4	59.9	59	63.9	61.6	62.4	62.7	54.0
					Ca = 6	; Al+S	+Cl+S	i = 5; r	ecalcul	ated fo	r 11 ca	tions					
Si ⁴⁺	0.2	0.2	0.2	0.4	0.2	0.2	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.0	0.0	0.1	
Cl^+	0.1	0.1	0.2	0.1	0.0	0.0	0.0	0.0	0.1	0.3	0.1	0.1	0.1	0.1	0.1	0.1	
Al ³⁺	2.2	2.1	2.0	2.0	2.0	2.0	2.0	2.1	2.1	2.0	2.1	2.0	2.1	2.1	2.1	2.2	2.0
S ⁶⁺	2.6	2.5	2.5	2.4	2.9	2.9	2.9	2.7	2.7	2.7	2.9	2.9	2.8	2.9	2.7	2.8	3.0
Ca ²⁺	6.0	6.1	6.0	6.0	5.9	5.9	5.9	6.1	6.0	5.8	6.0	6.1	6.1	6.1	5.8	6.0	6.0
Σcat	11.0	11.0	10.9	11.0	11.0	11.0	11.0	11.0	11.0	10.8	11.2	11.2	11.2	11.2	10.6	11.2	11.0

TABLE 6: Chemical composition of ettringite individuals present in pores of deteriorated concretes with rhyolite aggregate (sample 7 and 8) and andesite aggregate (sample 6). Analysed by R. Čonjaková.



Figure 1: Geological scheme of the stratovolcano near Banská Štiavnica.



Figure 2: Macroscopic appearance of concretes with rhyolite and andesite aggregates.



Figure 3: Stellerite with a rim of layered gels (A - Sample no. 8), pores filled with ettringite lined with new-formed alkali feldspars (B - Sample no. 8) and ACR gels next to stellerite (C - Sample no. 4). BSE, Cameca SX 100, photo by R. Čopjaková.



Figure 4A: Distribution of Ca, Al, Si, Mg, K, S, Fe, Na, K and Cl - stellerite, lined with gels containing hydrocarbonates microliths. Analyzed by R. Čopjaková.



Figure 4B: Distribution of Ca, Al, Si, Mg, K, S, Fe, Na, K and Cl - zonal gels between new-formed alkali feldspars and pore filled with ettringite (Sample no. 8). Analyzed by R. Čopjaková.



Figure 4C: Distribution of Ca, Al, Si, Mg, K, S, Fe, Na, K and Cl - partly recrystallized ACR gels (Sample no. 4), partly replaced by stellerite. Analyzed by R. Čopjaková.



Figure 5: Sergeevite, manasseite (low birefringent, around stellerite), sjögrenite (red-brown), pore filled with stellerite, tobermorite replacing gel (BSE). Olympus BX 51 polarising microscope, Photo M. Gregerová. Analyzed by M. Dosbaba.



Figure 6: Calcite encrustations on the concrete surface. Photo M Gregerová.



Figure 7: Corrosion of calcite crystals' surface. BSE, EDX. Analysed by R. Škoda.



Figure 8: Needle-like ettringite-thaumasite crystals. BSE, EDX. Analysed by R. Škoda.