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POZZOLANIC ACTIVITY OF VOLCANIC TUFF AND SUEVITE: EFFECTS OF CALCINATION

E. Liebig[1] and E. Althaus
Mineralogisches Institut der Universität Karlsruhe, Kaiserstraβe 12, D-76128, Karlsruhe, Germany

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ABSTRACT

The pozzolanic activity of two volcanic tuffs (Rhenish Trass) and the impact breccia Suevite (Bavarian Trass) were studied experimentally. Analcite, phillipsite and smectite present in the pozzolanas were investigated seperately. All samples were calcined at 500 and 800°C, respectively. Both the untreated and calcined materials were mixed with a $Ca(OH)_2$ solution, CH, and with a lime mortar. The amounts of Ca combined by pozzolanic reactions and also of Al released into the CH solution were taken as indicators for the pozzolanic activity. They are higher in the tuff samples than in suevite, which results in a higher compressive strength of mortars containing tuff. Heating to 800°C increases the pozzolanic activity and mortar strength of suevite mixtures. The latter is attributed to the activation of smectites present in suevite and the reduction of their swelling capacity and their high specific surface area. The effect of heating on the tuff samples is indifferent or even negative. Only the tuff rich in phillipsite shows improved pozzolanic properties after heat treatment at 500°C. In contrast to analcite, phillipsite can be activated by calcination. *© 1998 Elsevier Science Ltd*

Introduction

The preparation of hydraulic lime mortars using natural pozzolanas of volcanic origin has a long tradition and its use is frequently observed, for instance in Roman buildings. Particularly in the restoration of historical buildings pozzolana-lime-mortar is often applied with the intention of the chemical and techological properties of the repair mortar beeing in harmony with the historic materials of ancient buildings.

Different types of natural pozzolanas are quarried in Germany. Volcanic tuffs of comparatively young—quarternary—age from the Eifel volcanic area (so-called "Rhenish Trass") have preserved mineral components able to react with the soluble calcium of lime mortars. The pozzolanic property of volcanic tuffs from different localities as investigated by several authors (1–8) has been attributed to their high content of amorphous volcanic glass and postvolcanic minerals. The volcanic tuffs contain zeolites, which have pozzolanic properties

[1]To whom correspondence should be addressed.

TABLE 1
Mineral compositions of the pozzolanas.

material	minerals
tuff A	glass, analcite, mica, feldspar, quartz
tuff P	glass, phillipsite feldspar, mica, quartz
suevite	glass, quartz, feldspar, smectite, muskovite/illite

in their natural stage or after heat treatment (3–8). The "Bavarian Trass" is a material not of volcanic origin but formed by the impact shock of a large meteorite that produced the Ries crater. The rock known as "suevite" consists essentially of silicate glass mixed with shocked mineral and rock fragments and contains secondary smectites in considerable amounts. The phases are in a reactive stage and form with $Ca(OH)_2$ and H_2O Ca-silicate and -aluminate hydrates which are very similar to those produced with volcanic tuff or those known from hydraulic lime or cement. The pozzolanic activity of smectites can be improved significantly by calcination (9–11).

The pozzolanic properties of many materials (e.g. zeolites and clay minerals) can be changed dramatically by heat treatment. The same is assumed to be true for both volcanic and impact trass, but very little data exist so far on the influence of calcination on these materials. It is also well known that, by reaction with liquid phase, soluble components such as alkalies might be mobilized from the pozzolanas in sometimes considerable amounts, and therefore give rise to the formation of inorganic species entered in the liquid phase.

A study was performed, accordingly, on the effect of heat treatment on the pozzolanic activity and the alkali mobility of both volcanic and impact trass materials. The pozzolanic activity of analcite, phillipsite and smectite present in the pozzolanas was also investigated separately.

Materials and Methods

The two volcanic tuffs (tuff A and tuff P) used in this study come from different localities within the Eifel Trass mining region while the suevite was recovered from a quarry close to the Nördlinger Ries in Germany. All these rocks have high contents of about 50% to 60% of amorphous material. Mineral and chemical compositions of the pozzolanas are listed in Table 1 and 2, respectively. From the suevite rock, the fraction of minerals < 2 μm which consists

TABLE 2
Chemical compositions of materials investigated.

material	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	H_2O	CO_2	Σ
tuff A	54.09	18.14	4.98	1.28	2.59	3.65	4.38	8.23	1.16	98.50
tuff P	54.49	16.41	4.97	1.6	4.21	0.97	5.06	11.5	0.85	100.1
analcite	52.87	23.89	1.18	0.01	0.05	13.03	0.78	7.89	0.05	99.75
phillipsite	52.05	18.09	0.01	0.02	0.1	5.33	7.42	16.8	0.07	99.89
suevite	64.36	14.65	4.23	1.84	2.14	1.92	2.15	6.85	0.7	98.84
smectite of suevite	52.25	19.09	8.0	1.8	2.06	0.52	1.04	16.4	0.74	101.90

TABLE 3
Water-binder ratio of the pozzolana-lime mortars.

pozzolana	water-binder ratio
tuff A	1.21
tuff A 500*	1.20
tuff A 800	1.20
tuff P	1.22
tuff P 500	1.22
tuff P 800	1.20
suevite	1.29
suevite 500	1.22
suevite 800	1.20

* Numbers indicate calcination temperature.

exclusively of smectite was separated and investigated separately. The properties of the zeolite minerals analcite and phillipsite, the main mineral components of the tuffs, were also examined. In the fine-grained tuffs, however, a separation of individual phases was not possible. For the experiments analcite from Flinders, Australia and phillipsite from Nidda, Germany were used.

Experimental Methods

Samples were calcined at 500° and 800°C for 5 h. Changes in mineral composition and in specific surface area were studied by XRD, DTA and BET, respectively. The pozzolanic activity of the samples was determined by two different methods:

1. Samples powder, both untreated and calcined, was added to a saturated solution of $Ca(OH)_2$ (CH) in order to determine the extent of its reaction with CH to form Ca-Al/Si-hydrates. The fixation of Ca by the solids was determined after 90 days by measuring the Ca concentration in the CH solution. The Al and Si concentrations brougt into the solution by the pozzolanas were determined, as well as the concentrations of soluble Na and K. Concentrations of Ca, Na and K were determined by ion chromatography (HPLC), and Si and Al concentrations were measured by spectrophotometric method. The solid reaction products of the CH-pozzolana-mixtures were identified by XRD and SEM.
2. The compressive strength of pozzolana-lime mortar prepared with both untreated and calcined material was examined. The lime-sand ratio of the reference lime mortar was 1:3 by volume. Accordingly, a mass ratio of 1:7.6 follows. If a pozzolana was added, 50 wt % of the lime was replaced by the pozzolana. Water was added to produce a workable mortar. In order to achieve a similar degree of flow for all mixtures, the water-binder ratio varied between 1.20 and 1.29 (Table 3). Standardized prisms $2 \times 2 \times 8$ cm in size were prepared and aged in the mould for 7 days at 20°C. After removal from the moulds, they were stored at 20°C and 85% relative humidity. Compressive strength tests in a uniaxial testing apparatus were performed 28 days after the production of the mortars

TABLE 4
Specific surface area (BET) of the pozzolanas.

	specific surface area of the untreated sample in m^2/g	specific surface area after calcination at 800°C in m^2/g
tuff A	31.9	16.4
tuff P	35.2	17.2
suevite	51.5	19.1
smectite of suevite	90.5	16.6

following the German Standard DIN 18555–3. Strength results reported here are averages of five tests. The maximum coefficient of variation for strength was 7%.

Results and Discussion

Mineral and Physical Properties after Heat Treatment

Heat treatment up to 800°C leads to structural and chemical changes in the materials. Concerning this, the emission of water is the decisive process. The zeolites of the volcanic tuffs lose their crystal water during heat treatment, but analcite and phillipsite react differently. Analcite keeps its crystal structure even after loss of water, while phillipsite breaks down to metaphillipsite at temperatures well below 500°C. At temperatures above 350°C, when dehydration is complete, a feldspar phase begins to form (12) that is more obvious at 500°C. The smectite of the suevite loses its interlayer water between 100° and 200°C, while dehydroxilation takes place at higher temperatures and is complete at about 720°C. After heat treatment at 800°C the (001) d-spacing decreases, indicating a collapse of the crystal lattice parallel to this plane. Heated smectites have a higher pozzolanic activity than the untreated minerals (9–11). Illite and mica occuring in all three rocks dehydroxilate at 800°C, but their structures do not collapse. Investigations by He et al. (13) have shown that illite has a low pozzolanic activity, which can only slightly be enhanced by calcination up to 800°C. Mica minerals like muscovite and phlogopite do not react with $Ca(OH)_2$ solution even after heat treatment (14,15). The other mineral phases of the three rocks are not influenced by heating up to 800°C. Even the vitreous components do not recrystallize.

Heat treatment reduces the specific surface area of the samples (Table 4). The suevite shows this effect paricularly distinctly because of its high content of expandable smectite.

Pozzolanic Activity of the Materials and Compressive Strength of Pozzolana Lime Mortars

A decrease in the Ca contents of the $Ca(OH)_2$-solutions has been registered in all experiments involving the different solid samples. This indicates the formation of Ca-$\underline{S}$i/Al-hydrates. The following reaction products have been identified: C-S-H, C_4AH_{13}, $C_4A\bar{C}H_{11}$, and C_2ASH_8 (abbreviations: C, CaO; A, Al_2O_3; S, SiO_2; H, H_2O; $\bar{C}$, CO_2; C-S-H, nearly amorphous calcium silicate hydrate with variable chemical composition). Formation of C-S-H takes place in all samples taking up Ca. The different Al-bearing Ca hydrates occur in various

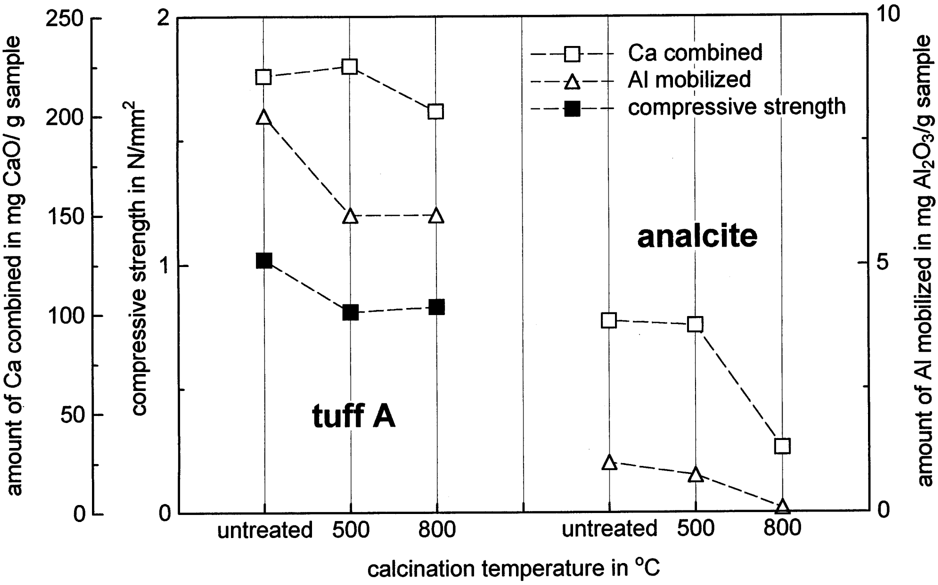

FIG. 1.

Amounts of Ca combined and of Al mobilizied from untreated and caclined tuff A and analcite in a saturated $Ca(OH)_2$ solution after 90 days. Compressive strength of mortars containing untreated and calcined tuff A.

proportions. No correlation has been recognized between the types and the amounts of reaction products and the Al concentrations in the CH solution. The Al and Si ions required for the formation of the Ca-Si/Al-hydrates are provided by the pozzolanas, and an excess of dissolved Al has been detected in the solutions. Dissolved Si was not found in any solution, but Si bearing solid reaction products have been observed instead.

The addition of the different untreated and calcined pozzolanas to lime mortars distinctly influences its compressive strength (Figs. 1–3). A lime mortar prepared without addition of pozzolanic material has a compressive strength of 0.8 N/mm^2. Mixing with the different pozzolana powders results in sometimes drastic changes.

Tuff A

Calcination does not impove but rather reduces the pozzolanic activity of tuff A. The untreated sample takes up 220 mg CaO/g sample and releases 15.0 mg Al_2O_3/g sample (Fig. 1). Heat treatment at 800°C results in a decrease of 8.2 and 21.3%, respectively, compared to the untreated sample. The behaviour of the tuff is due to the properties of its main mineral phase, analcite. Analcite reacts to heat treatment with reduced pozzolanic activity. The amounts of Ca combined and of Al mobilized decrease with increasing calcination temperature (Fig. 1).

In correlation with the parameters indicating the pozzolanic activity, the compressive strength of the mortar prepared with the untreated tuff attains the highest value. With untreated tuff A the strength of the lime mortar is increased to 1.02 N/mm^2 (Fig. 1). The

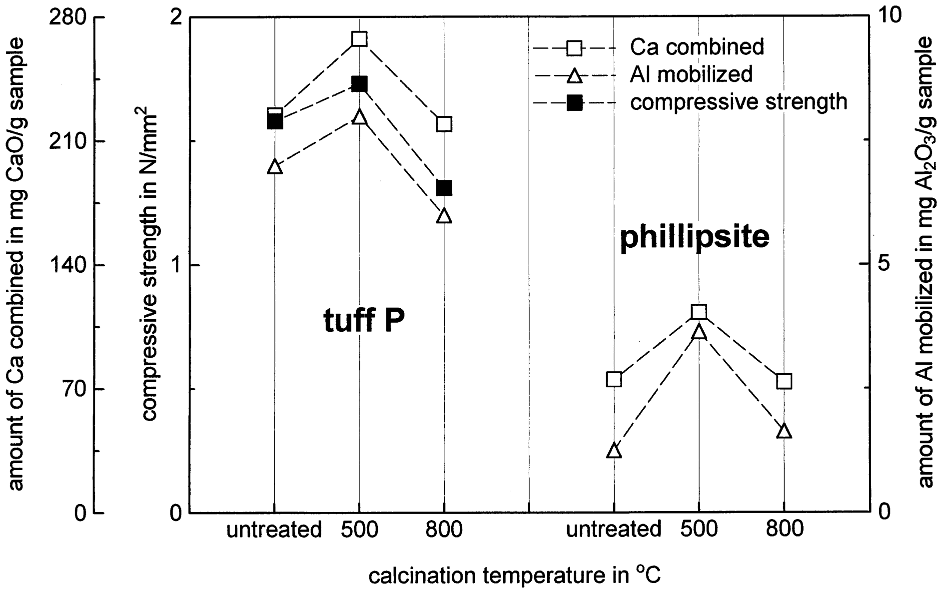

FIG. 2.

Amounts of Ca combined and of Al mobilizied from untreated and calcined tuff P and phillipsite in a saturated $Ca(OH)_2$ solution after 90 days. Compressive strength of mortars containing untreated and calcined tuff P.

addition of heat-treated material reduces it to 0.82 N/mm^2 regardless of the calcination temperature.

The amounts of Na and K released by the untreated tuff in CH solution are 32 mg Na_2O/g sample and 29 mg K_2O/g sample, respectively (Fig. 4). The amounts of mobile alkali are not influenced significantly by heat treatment.

Tuff P

Tuff P reacts to heat treatment in a different way. The pozzolanic activity of tuff P can be improved by calcination at 500°C. The untreated tuff P takes up 225 mg CaO/g and releases 13.2 mg Al_2O_3/g to the solution (Fig. 2). Both parameters increase with heat treatment at 500°C (19.5% and 13.3%, respectively). Calcination at 800°C, however, results in a decrease of reactivity. The properties of tuff P are strongly influenced by the thermal behaviour of its main mineral phase, phillipsite. Phillipsite becomes a highly reactive product when calcined at 500°C, but by heat treatment at 800°C it is transformed to a stable feldspar phase with low pozzolanic activity (Fig. 2).

In agreement with the valuation of pozzolanic activity, the addition of 500°C calcined tuff P results in the highest strengths of all tested pozzolanas. With untreated material, the strength is increased to 1.58 N/mm^2 (Fig. 2), almost twice that of a pozzolana-free mortar. Heating to 500°C further increases the strength to 1.73 N/mm^2, while treatment at 800°C reduces it again to 1.31 N/mm^2.

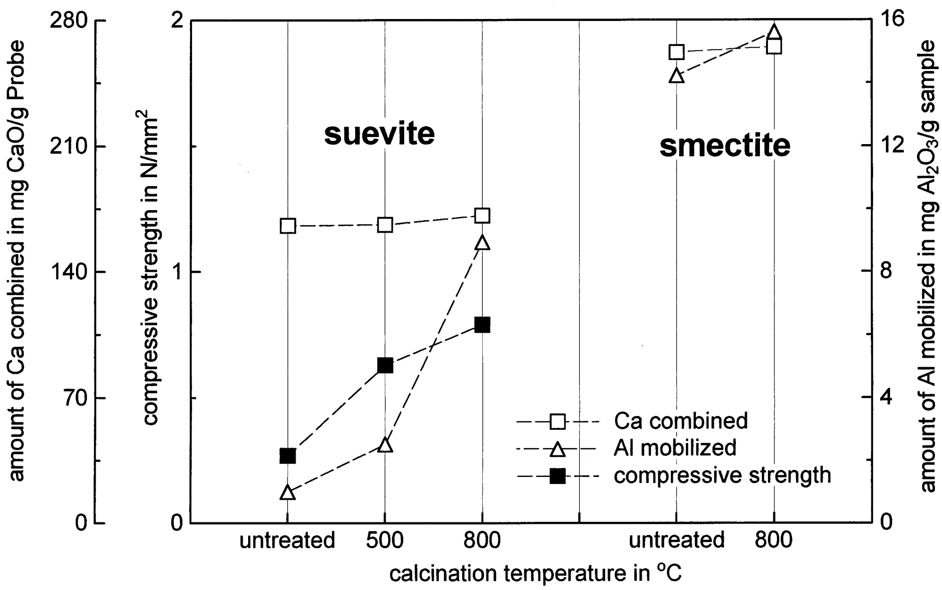

FIG. 3.

Amounts of Ca combined and of Al mobilizied from untreated and calcined suevite and smectite in a saturated $Ca(OH)_2$ solution after 90 days. Compressive strength of mortars containing untreated and calcined suevite.

K mobilization of tuff P is comperatively high (70.9 mg K_2O/g sample, Fig. 4) because the highly potassic mineral phillipsite (Table 2) is unstable in calcium hydroxid solutions.

Suevite

The suevite has lower a pozzolanic activity than the volcanic tuffs. However, its reactivity can be improved by heat treatment. The untreated sample takes up 166 mg CaO/g sample (Fig. 3). Calcination at 800°C results in an increase of 4.2%. The potential to release Al in the CH solution is affected much more significantly by calcination (from 1.0 mg to 7.9 mg Al_2O_3/g sample, Fig. 3). The pozzolanic activity of the suevite is not only due to the reactivity of the vitreous component. The smectite of the suevite is also very reactive. Amounts of Ca taken up and Al released from smectite (262 mg CaO and 14.2 mg Al_2O_3/g sample) are significantly higher than in the bulk sample. It is to be recognized, however, that because of its high specific surface area (Table 4) the untreated smectite is also able to adsorb Ca in considerable amounts without any pozzolanic reaction. This implies that the pozzolanic activity of the untreated suevite and smectite might be lower than indicated by the Ca combination. Calcination at 800°C improves the reactivity of the smectite (Fig. 3).

In spite of its pozzolanic activity, the addition of untreated suevite produces a mortar with very low compressive strength (0.27 N/mm^2, Fig. 3). The latter can be understood if the properties of the smectite present in suevite are being taken into acount. The swelling of the untreated smectite reduces the mechanical stability of the mortar. Furthermore, the high specific surface area of the smectite results in a water-binder ratio which is rather high

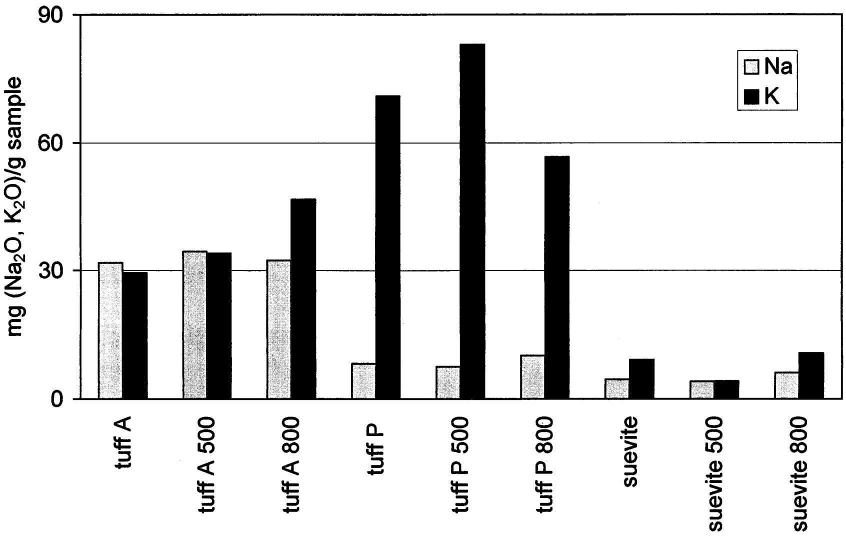

FIG. 4.
Amounts of Na and K mobilized from the untreated and calcined pozzolanas in $Ca(OH)_2$ solution after 90 days. Sample abbreviations: numbers indicate calcination temperature.

compared to that of mortars containing heat-treated suevite or volcanic tuffs (Table 3). The compressive strength of the mortar prepared with calcined (800°C) suevite increases to 0.79 N/mm^2 (Fig. 3). The suitability of the suevite as a pozzolanic additive can be improved significantly by heat treatment because of the activation of the smectite as well as the reduction of its swelling capacity and its specific surface area (Table 4).

Na and K contents of the solutions in contact with untreated and calcined suevite samples are rather low (Fig. 4), and variations due to heat treatment are negligible.

Conclusions

The untreated volcanic tuffs investigated have considerably higher pozzolanic activities than the untreated suevite, leading to higher compressive strengths of the pozzolana-lime mortars. They release, however, to the mortar liquid rather high amounts of dissolved Na and K. The advantage of the suevite is its low Na and K content.

The reactivity of the pozzolanas can be increased by heat treatment if they contain components which can be activated by calcination. The phillipsite of tuff P and the smectite of the suevite have this particular property. The pozzolanic activity of the suevite calcined at 800°C increases considerably. Added to a lime mortar it triplicates the compressive strength compared to untreated material. For volcanic tuff, calcination is less favourable since it can reduce the mortar's compressive strength. Depending on their mineral composition, various tuffs respond differently to heating.

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