

HYDRAULIC BINDER FROM MECHANO-CHEMICALLY ACTIVATED PUMICITE

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Pumicite is a granular, light gray, sandy rock, with particles including many closed or open pores. It is an aqueous silicate glass arising during volcanic activity (rhyolite), from gaseous silicate melt blown up with bubbles by gases leaving upon cooling, and the solidifying glass is broken up to particles by inherent stresses. Throughout the geologic periods, the material has kept its metastability, thus, most of its mass is still amorphous.

Significant pumicite deposits are found in the *West-Mátra* and *Zemplén mountains* in Hungary. These are partly overlying kieselguhr deposits, partly contacting kaoline masses, decisive for their impurities (quartz, zeolite, kaoline, feldspar).

The two test samples to be discussed are pumicites from *Szurdokpüspöki* and from *Bodrogszegi* (marked SP and BP, respectively), with major chemical, mineralogical and grading characteristics compiled in Table I.

Pumicite has been utilized for plastering, grinding or scouring powder or filtering materials, in minor quantities compared to the available resources. Not sooner than recently started an extensive technology research on the industrial utilization of pumicite, initiated by the *Central Geological Office* (*Dr. Gyula Varju*), resulting in several, partly patented methods, among them that developed at the *Technical University, Budapest*, concerned with the production of a hydraulic binder [1]. The procedure relies on the mechano-chemical activation of pumicite, that is, artificial enhancement of its chemical reactivity by means of intensive mechanical force effects, in the actual case by intensive grinding (supergrinding).

Mechano-chemical activation significantly improves the setting ability of pumicite-lime or pumicite-cement systems, so that aqueous pastes from these systems harden to high-strength cement — even under water.

The setting depends on the method and grade of previous mechanical activation of pumicite, as seen in Fig. 1 where the setting of two pumicite samples ground in vibrating mill, that is, compressive strengths of the hardened mortars have been plotted vs. grinding (activation) time. Prolongation of the grinding (activation) time is seen not to increase the setting ability beyond

Table I

Chemical, mineralogical and morphological characteristics of raw pumicite samples

Chemical composition %	Sample SP	Sample BP
SiO ₂	71.7	71.3
Al ₂ O ₃	12.6	14.3
Fe ₂ O ₃	1.35	1.19
CaO	3.33	1.78
MgO	1.98	0.00
K ₂ O	2.97	2.91
Na ₂ O	1.02	1.15
SO ₃	1.24	0.74
Heating loss	5.32	5.49
Silicate modulus	5.14	4.60
Amorphous glass (%)	86	80
Quartz (%)	10	10
Feldspar, zeolite, kaoline (%)	4	10
Density (gml ⁻¹)	2.265	2.304
Solid density of particles (gml ⁻¹)	1.53	1.78
Grading: below 200 μm (%)	95.9	81.7
63 μm (%)	77.3	27.3
46 μm (%)	54.7	7.8
Particle porosity	0.33	0.11
Specific surface (m ² g ⁻¹)	31.1	21.3

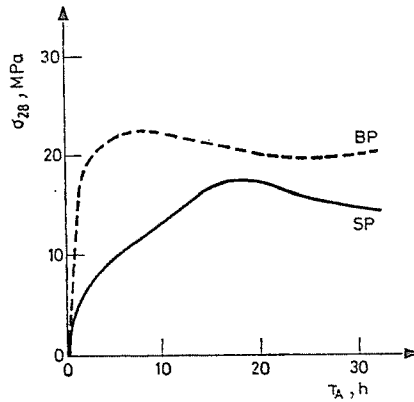


Fig. 1. Compressive strength σ_{28} of pumicite-lime hydrate mortars water cured for 28 days vs. grinding time τ_A in a vibrating mill

limits, an excessive grinding time may even reduce the setting ability. This phenomenon itself is a hint to the likelihood of secondary procedures harmful to the final product to occur in mechanical activation, besides of primary processes improving the setting ability. Unacquaintance with these harmful or proficient processes intrigued us to explore them.

1. Experimental fundamentals

Grinding in general can be considered as a mechanical activation, thus, as an operation resulting in the increase of free energy of solid systems.

Grinding reduces the setting energy between atoms of a solid. Change of the setting energy ΔE_K is composed of the reduction of the lattice energy ΔE_R and the increase of the surface energy ΔE_F [2]:

$$\Delta E_K = \Delta E_R - \Delta E_F. \quad (1)$$

Three cases of mechanical activation can be distinguished according to the variation of the setting energy:

a) Setting energy variation is due exclusively to the specific surface increase — thus, particle size reduction — the lattice energy remains unaltered:

$$\Delta E_K = - \Delta E_F = - E_\gamma \Delta S \quad (2)$$

E_γ , being the unit surface free energy, and ΔS the specific surface increase.

This is the case of “mechanical dispersion”.

b) Besides of the increase of the specific surface, surface texture alterations modify the free energy per unit surface, the surface potential E_γ :

$$\Delta E_K = - \Delta(E_\gamma \cdot S). \quad (3)$$

This kind of mechanical activation is termed “surface activation”.

c) Finally, if the above alterations accompanied by change of the crystal structure concomitant to residual deformations and bond disruptions reduce the lattice energy, the setting energy changes by:

$$\Delta E_K = \Delta E_R - (E_\gamma \cdot S). \quad (4)$$

This most general case is that of “mechano-chemical activation”.

Familiarity with even the part-processes of mechano-chemical activation, the most general of the cases, would require to describe the state of the activated system from the aspects of mechanical dispersion surface activation, internal crystalline properties and chemical processes. Actually, however, direct determination of E_R , E_γ and S is mostly — hence also for pumicite — impossible, their changes can only indirectly be demonstrated. Chemical reac-

tivity has been described by the rate of an appointed reaction under uniform circumstances.

1.1 *Setting energy variation* ΔE_K was concluded on from solution heat measurements.

Solution heat was determined in a special calorimeter heated to $60 \pm \pm 0.3$ °C, applying a NaOH solvent of 1 mol/l concentration, and assuming:

$$(Q_l - Q_l^0) \cong \Delta E_K \quad (5)$$

where Q_l and Q_l^0 are solution heats of grinds activated and not activated, respectively.

1.2 *The rate of mechanical dispersion* is defined — in conformity with Eq. (2) — by the variation of the specific surface S .

Nevertheless, for most of the grinds, the concept of specific surface is difficult to realize. Namely, in the grind bulk, beside primary particles, porous in themselves, there is a great variety of aggregates, containing, beyond pores in the primary particles, also open and closed pores resulting from aggregation. Specific surface values are influenced by the surface system of the bulk affected by the actually applied testing method.

Our investigations referred to two kinds of surfaces typical of the specific surfaces of grinds [3]:

- specific surface determined by vapour adsorption, closest approximation of the total surface area of primary particles (dispersity degree Ω_v);
- specific surface determined from the gas permeability of the grind bulk, representing mainly the outer surface of secondary particles, involving the voids system of the bulk (grinding fineness ω).

Besides, an earlier developed method [3] was applied to determine the volume of closed pores in particles of the bulk (particle porosity ε_0).

1.3 *Surface activation* was concluded on from the variation of the vapour adsorption energy E_v of the system, assuming unambiguous logic relation between variations of E_v and of the surface free energy E_F .

Adsorption energy may be considered as product of adsorption potential ψ_v by the specific surface:

$$E_v = \psi_v \cdot \Omega_v, \quad (6)$$

both magnitudes can be determined from vapour adsorption isotherms [3].

1.4 *The degree of mechano-chemical activation* may theoretically be deduced from the variation of lattice energy i.e., of chemical potential, maybe the activated systems could be described in terms of variation of the crystalline structure (amorphization) and of the increase of reactivity.

Grinding changes in the glassy structure of the *a priori* amorphous pumicite could, however, not be demonstrated by material structure testing methods usual in silicate chemistry. For instance, X-ray tests (made by the late *Dr. Miklós Udvardy*) failed since diffractograms of pumicite, X-ray amorphous in its main mass, containing little silica and feldspar, did not exhibit essential changes after grinding but only decrease of reflexions of crystalline impurities (Fig. 2).

Again, IR absorption tests (made by *Dr. Klára Jónás*) were negative. Adsorption curves were practically identical for native and for ground pumicites (Fig. 3).

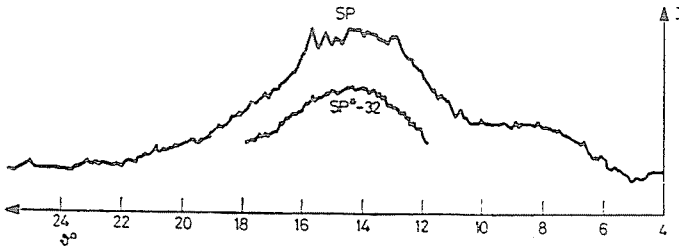


Fig. 2. Pumicite diffractogram. SP: original; SP*-32: activated



Fig. 3. IR spectrum of pumicite

Although derivatograms could demonstrate setting energy variations of water bound in vitreous structures (Fig. 4), these signals were insufficient to penetrate into silicate structure changes, imposing to apply unusual test methods. The methodology being rather unusual, tests have been extended to silicate minerals other than pumicite to help interpretation of measurement results.

1.4.1 Oxygen compactness. Vitreous silicate structures are approximately described by the "oxygen volume" suggested by STEVELS [4], space occupied by a single oxygen atom in the silicate skeleton, to be calculated from the oxide-chemical composition and density of glass. The relation between

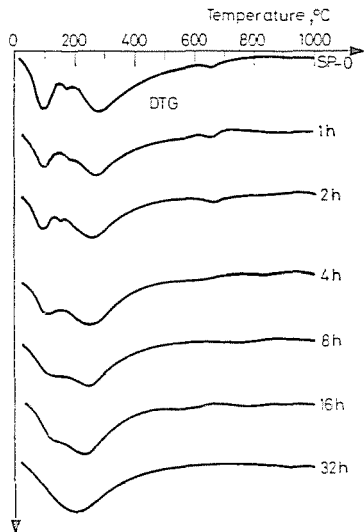


Fig. 4. Derivatograms of pumicite samples in original condition and after mechanical activation for different times

oxygen volume and macroscopic characteristics — refractivity, strength, etc., — of glasses of different compositions has been pointed out by NÁRAY-SZABÓ [5].

Along these lines, the silicate structure in grinds is approximately described — rather than by the space occupied by a single oxygen atom — by the “oxygen compactness” referring to the complete silicate skeleton, calculated as:

$$\xi_{ox} = \frac{v_{ox} n_{ox}}{v_{sz}} = \frac{v_{ox} \sum n'_{ox}}{100} \cdot \rho = 1,03 \cdot 10^{-25} \cdot \rho \cdot n_{ox} \quad (7)$$

where $n_{ox} = \sum n'_{ox}$, number of oxygen atoms in 100 g of silicate, calculated from the chemical (oxide) composition. Calculation steps and the applied conversion factors have been compiled in Table II, illustrated on an example;

v_{ox} — volume of a single oxygen atom. In the case of an atomic radius of 0.135 nm [6]: $1,03 \cdot 10^{-23}$ ml;

ρ — silicate density measured in a pycnometer (g/ml);

v_{sz} — volume of 100 g of silicate (ml).

1.4.2 Dielectric constant and depolarization rate. The dielectric constant of silicate grinds was determined by an earlier published method (dispersing the grind in a paraffin specimen) [3]. Basic measurements were made on samples dried at 110 °C (DK) then the samples got heated and dielectric

Table II
Multipliers for calculating the oxygen compactness (illustrated)

Oxide composition %		Multiplier	n'_{oz}
SiO ₂	71.3	20.05×10^{21}	1429.66×10^{21}
Al ₂ O ₃	13.9	17.71×10^{21}	246.17×10^{21}
Fe ₂ O ₃	1.35	11.32×10^{21}	15.28×10^{21}
FeO	0.15	8.37×10^{21}	1.26×10^{21}
TiO ₂	0.00	15.07×10^{21}	0.00
CaO	1.90	10.72×10^{21}	20.37×10^{21}
MgO	0.10	14.93×10^{21}	1.49×10^{21}
K ₂ O	2.97	6.38×10^{21}	19.95×10^{21}
Na ₂ O	1.02	9.69×10^{21}	98.84×10^{21}
Heating loss	6.67	33.42×10^{21}	222.91×10^{21}
SO ₃	0.02	22.52×10^{21}	0.45×10^{21}
99.38			$n_{ox} = 2,055.72 \times 10^{21}$
$\rho = 2.265 \text{ g/ml}$			$\alpha_{ox} = 0.467$

constant DK_i of the hot solids determined. Hot temperature depended on the leaving temperature of the constitutional water of silicate [7]. In every case, heating losses were determined by weighing ($w_i\%$).

Evaluation of measurement results followed the considerations below:

Mixing $w_i(g)$ of water to the heated sample would result, in conformity with the relationship of additivity [8], in a dielectric constant for the mix:

$$DK_t = v_i DK_i + v_v DK_v \quad (8)$$

where v_i and DK_i , v_v and DK_v are percentages by volume, and dielectric constants, of heated silicate and of pure water, respectively.

The effective dielectric constant DK of silicates is, however, mostly lower than that given by Eq. (8), since the silicate skeleton hampers the arrangement of water molecules in direction of the electric field. The ΔDK value obtained from

$$\Delta DK = \frac{DK_t - DK}{DK_t} \quad (9)$$

is termed the "depolarization degree".

1.4.3 Description of mechano-chemical activation in terms of Al-solubility. Chemical reactivity of mechano-chemically activated silicate systems

has been described — in conformity with [9 to 11] — in terms of the aluminium quantity dissolved in hydrochloric acid, the so-called Al-solubility.

Aluminium dissolved under defined test conditions — expressed in Al_2O_3 — has been referred to 100 g of sample α , % or to the total Al_2O_3 in the sample (l_{Al} %). Dissolution was made by boiling in a HCl solution of 1 mol for two hours. The dissolved Al_2O_3 was determined by complexometry.

The activation degree A_K can be expressed by the difference of solubilities between activated and non-activated silicate grinds:

$$A_K = \frac{l_{\text{Al}} - l_{\text{Al}}^0}{l_{\text{Al}}^0} \cdot 100. \quad (10)$$

1.4.4 Other solubility tests. Applying different solvents (HCl, NaOH, KOH, H_3PO_4), relative solubilities of chemical components of pumicite were separately determined.

1.4.5 Reaction of pumicite with lime. Composition of silicate gels arising during the hydraulic setting of aqueous pastes of silicate-lime systems, responsible for the hardening itself, are difficult to determine, not only because of the amorphousness of gels making them inaccessible to usual crystal chemistry methods for identification but also because there is no complete transformation during usual testing times, so that the hardened cement contains, beside reaction products, the original basic materials. The test was made by mixing the pumicite with different proportions of calcium hydroxide, adding 70% of sand and making a mortar of 0.65 w/c ratio cast into 2 cm side cubes. After water curing for 28 days, cube strength σ_{28} was determined. The composition of gel arising in the hydration process was concluded on from the following operations:

- CaO , Al_2O_3 and SiO_2 quantities (c , a , s) dissolved by two hours of boiling in HCl of 0.01 mol obtained by chemical analysis;
- unbound $\text{Ca}(\text{OH})_2$ quantities (c_H in terms of CaO) calculated from derivatograms;
- the CaCO_3 content (c_c in terms of CaO) determined by calcimetry;
- hydrating water quantities h assessed from mass losses between 22 °C and 440 °C indicated on derivatograms, corrected by the mass loss of neat pumicite in the mix.

Calcium oxide in the hydration product:

$$c_s = c - (c_H + c_c), \quad (11)$$

distribution of these oxides (C , A , S) in the hydration product:

$$C = \frac{c_s}{a + s + c_s}; \quad A = \frac{a}{a + s + c_s}; \quad S = \frac{s}{a + s + c_s}. \quad (12)$$

Hydrating water quantity referred to 1 mol of SiO₂:

$$H = \frac{h \cdot 60.09}{18 \cdot s} \quad (13)$$

2. Conclusions

2.1 *Mechanical dispersion* can be indicated by two kinds of state changes of the grind. One is increase of the dispersity degree Ω_v and grinding fineness ω of the system as a function of the grinding time (Fig. 5). ω grows generally, but not unambiguously, with the setting ability. This is illustrated in Fig. 6 presenting ball mill test results. Relative cube strengths referred to the compressive strengths of specimens made with neat portland cement have been plotted vs. grinding fineness, for different mill charges. Different setting abilities are seen to belong to the same grinding fineness.

The other state change is that of the grind morphology (Fig. 5): in grinding, first the porous particles are opened (ϵ_0 decreases while ω grows), but after 8 hours of grinding, aggregation of primary particles creates secondary particles containing inner pores (ϵ_0 increases, ω decreases). An intensive aggregation may reduce the overall specific surface Ω_v .

2.2 Surface activation (Fig. 7)

Vapour adsorption potential periodically varies vs. grinding time. Increase of ψ_v on freshly broken surfaces may be attributed to the development of high surface-active forces, and its decrease to the agglomeration of particles,

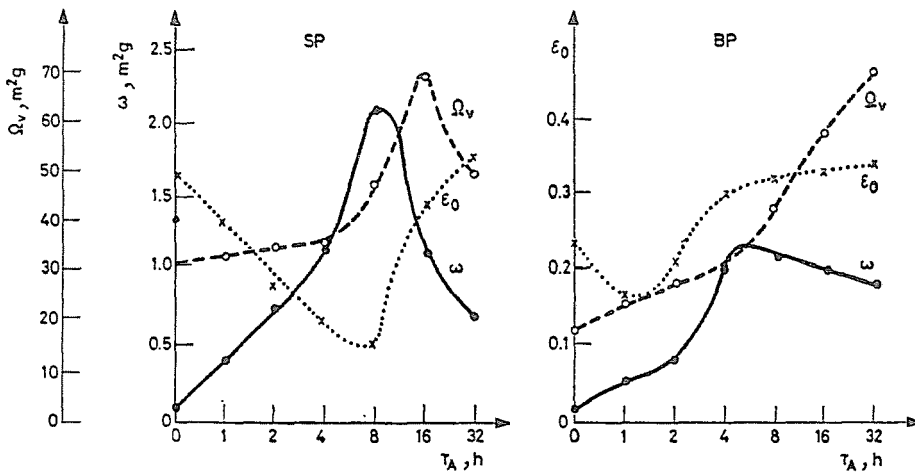


Fig. 5. Grinding fineness ω , "overall" specific surface Ω_v and particle porosity ϵ_0 vs. activation time τ_A

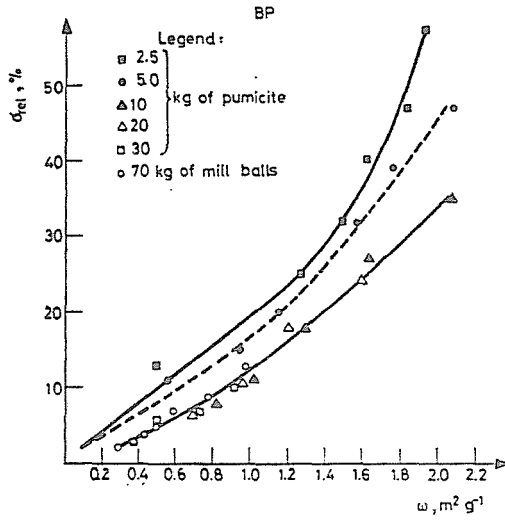


Fig. 6. Relationship between grinding fineness and setting. Ball mill grinding, charge: 70 kg of balls and indicated masses of pumicite

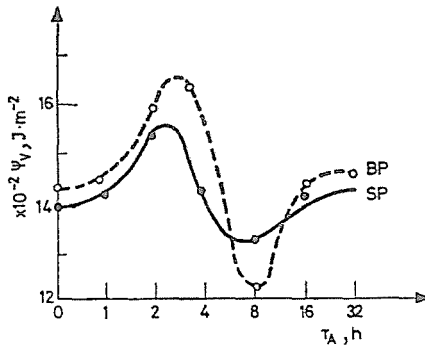


Fig. 7. Surface activation in terms of the vapour adsorption potential vs. activation time

or better, to the “cover effect”, that is, mutual overlapping of active surface centres of particles, desactivating the system to a degree.

2.3 Variation of the setting energy, as degree of mechano-chemical activation, follows Fig. 8. The involved overall surface activation $\Delta E_v = -\Delta(\psi_v \Omega_v)$ varied according to a maximum curve. ΔE_v peaked at a grinding time of 16 hours, just as did the setting ability in Fig. 1.

The specific power W_z utilized in the vibrating mill being known, mechanical activation has been described in terms of the following efficiencies (see upper diagrams in Fig. 8):

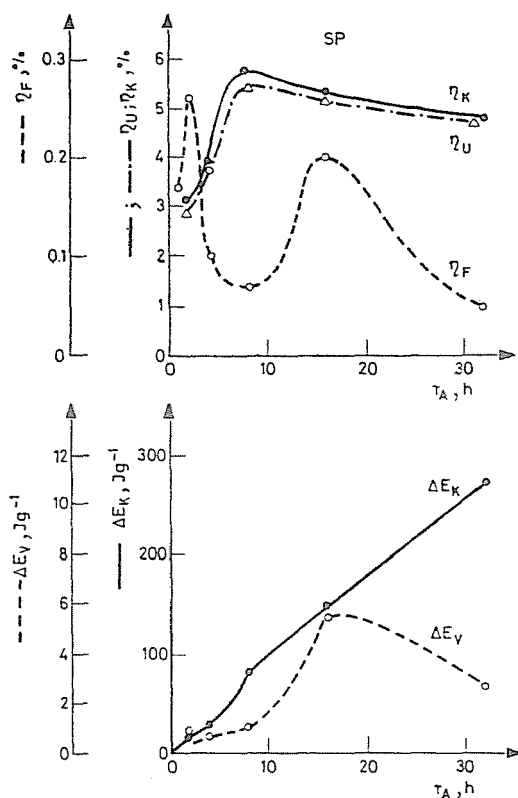


Fig. 8. Setting power and vapour adsorption energy ΔE_K and ΔE_v vs. activation time (bottom). Curves of mechano-chemical and surface activation efficiencies (top)

a) Efficiency of mechano-chemical activation:

$$\eta_K = \frac{\Delta E_k}{W_z} \cdot 100. \tag{14}$$

As little as 3 to 6 percent of input grinding power got utilized as total energy absorbed by the material, the other went lost for the process (as heat). η_K varies with the grinding time according to a maximum curve. Under experimental conditions, grinding in a vibrating mill achieved the maximum efficiency after 8 hours.

b) Surface activation efficiency:

$$\eta_F = \frac{\Delta E_v}{W_z} \cdot 100 \tag{15}$$

very low compared to η_K (as little as 0.1 to 0.2 percent).

c) Efficiency

$$\eta_u = \frac{\Delta E_k - \Delta E_v}{W_z} \cdot 100 \quad (16)$$

— especially for prolonged grinding — is near that of η_K . Thus, in prolonged grinding, energy absorbed by the pumicite is mainly spent on inner structural transformations.

2.4 *Investigations into silicate structural transformations* have led to the following conclusions:

a) Oxygen compactness ξ_{ox} vs. activation time grows up to a limit value, namely to about the oxygen compactness of cristobalite (Fig. 9).

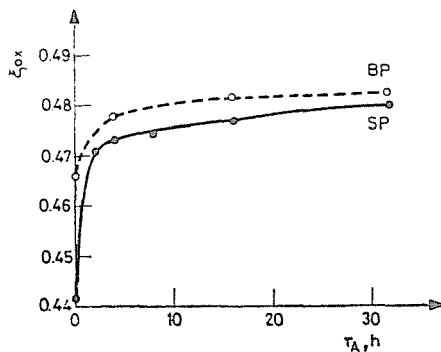


Fig. 9. Oxygen compactness vs. activation time

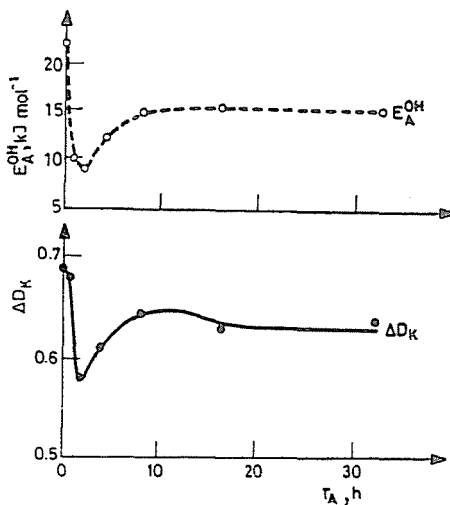


Fig. 10. Depolarization degree referred to water ΔD_K and thermal activation energy E_A^{OH} vs. activation time

Phase analysis permits to calculate the oxygen compactness of pure pumicite glass (0.453) growing to 0.469 after 32 hours of grinding.

At the same time, the oxygen compactness calculated for crystalline components (quartz, feldspar) goes decreasing.

b) Depolarization degree ΔD_K vs. grinding time follows a minimum curve (Fig. 10). The water release activation energy (E_A^{OH} in Fig. 10) calculated from the derivatograms by the method of CROISSANT and GARNAUD [12] follows a parallel trend. Both curves show the setting energy of water initially to decrease, then — after prolonged grinding — to increase.

c) Chemical activation degree A_K calculated from Al-solubility monotonously grows with the grinding time (Fig. 11). With increasing A_K , the setting ability grows to a limit value, beyond that — probably due to agglomeration — the setting force decreases. Chemical activation forwards setting activity only in occurrence of a favourable grind morphology. Pronenesses of the two pumicite samples to chemical activation significantly differed, in spite of similar chemical and mineralogical compositions.

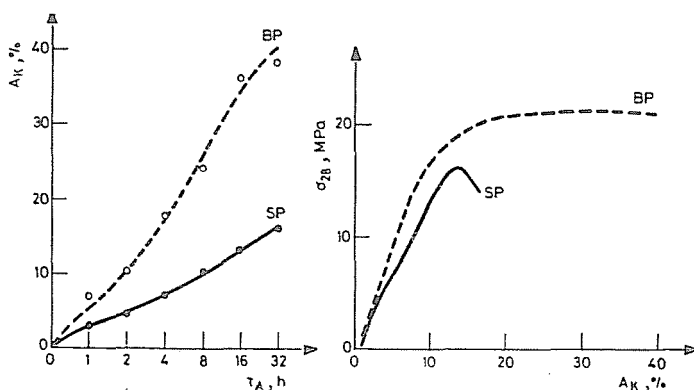


Fig. 11. Relationship between chemical activation degree A_K , setting power σ_{28} and activation time τ_A

2.5 *Alterations of the chemical reactivity* are indicated by variations in solubility according to different methods, and in relative proportions of the dissolved components.

Chemical solubility of pumicite much grew upon mechanical activation (Table III). Also Al present in non-activated and little activated pumicite is more readily dissolved in bases than in acids. Activation shifts this solubility towards acids (Fig. 12).

Also relative solubilities of some pumicite components change (Fig. 13). For instance, the ratio of lye-soluble SiO_2 to Al_2O_3 is higher in non-activated than in activated pumicite; the ratio of acid-soluble K_2O to Al_2O_3 grows after activation.

Table III

Parts to be dissolved in various acids and bases

Solvent	Sample SP		Sample BP	
	Original	Activated for 32 h	Original	Activated for 32 h
3% hydrochloric acid (100 °C 2 ^h)	2.1%	10.4%	0.9%	24.0%
4% caustic lye of soda (100 °C, 1/2 ^h)	18.8%	66.5%	10.5%	57.0%
20% potash lye (100 °C, 1/2 ^h)	21.6	60.5	10.7%	55.1%
Concentrated phosphoric acid (250 °C, 1/4 ^h)	86.4	100.0	82.4	100.0%

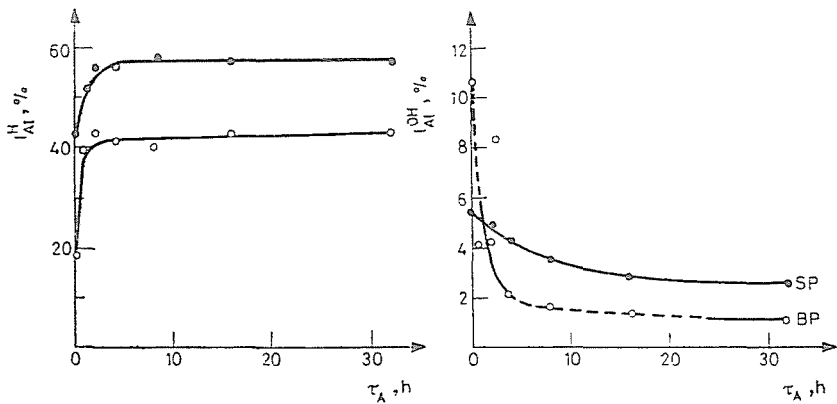


Fig. 12. Al-solubility for boiling in a lye l_{Al}^{OH} and its relation to Al-solubility in an acid $l_{Al}^{H^+}$ vs. activation time

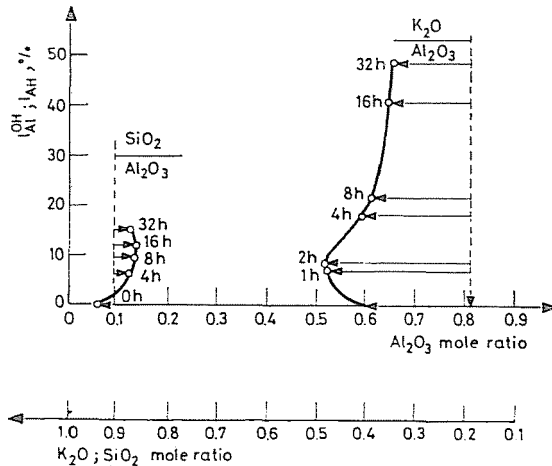


Fig. 13. Variation of ratios SiO_2/Al_2O_3 and K_2O/Al_2O_3 in the parts soluble in lye and in acid, respectively, after different activation times. Vertical arrows indicate SiO_2/Al_2O_3 and K_2O/Al_2O_3 ratios in the original pumicite

2.6 Reaction with lime hydrate. Relationship between chemical composition and setting power of hardened pastes of activated and non-activated pumicites made with different dosages of lime hydrate has been plotted in Fig. 14.

Diagram a) shows cube strength vs. Al_2O_3 dissolved from mortar specimens a. The setting power σ_{23} is seen to unambiguously increase for a soluble Al_2O_3 increase in the hardened cement.

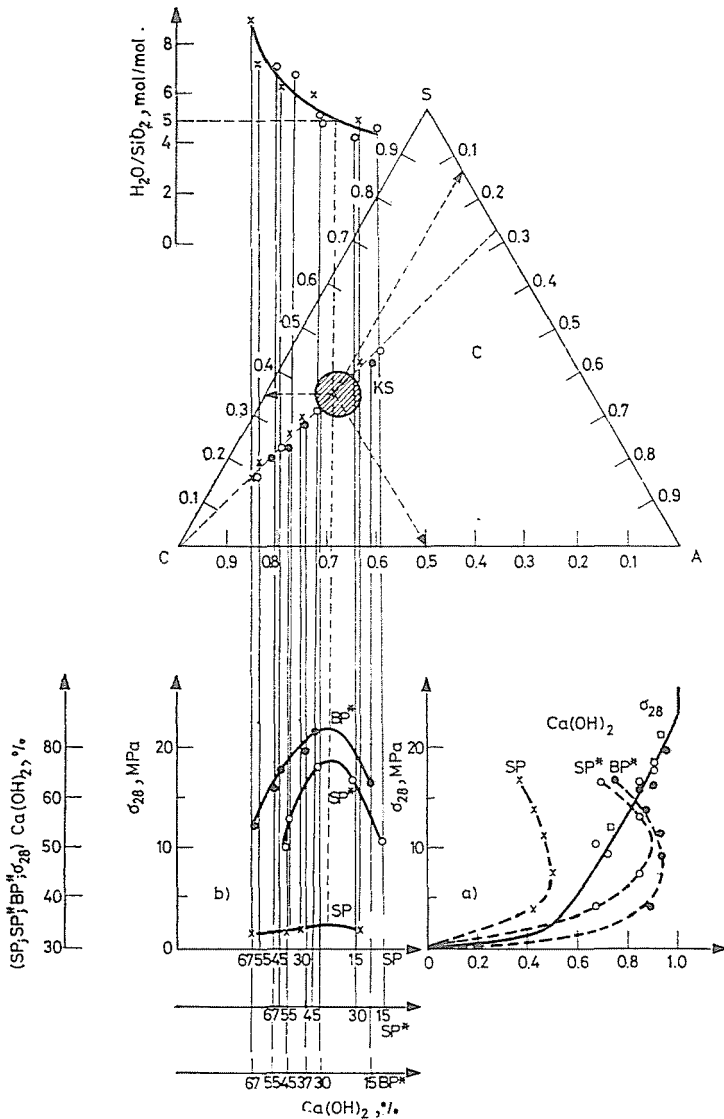


Fig. 14. Composition and setting power of hardened lime hydrate-pumicite-water systems. SP = non-activated, SP* and BP* = activated pumicites

This latter has two possibilities: either increase of the lime hydrate admixture to an optimum quantity, or mechanical activation of the pumicite (curves $\text{Ca}(\text{OH})_2$).

Relationship between lime hydrate admixture and cube strength has been plotted in diagram b). Lime hydrate content at the maximum strength depends both on the pumicite quality and on its preliminary mechanical activation degree (method).

Figure 14b) has been plotted relying on Fig. 14c) representing cement gel compositions in the triadic system $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$. Projecting plots in Fig. 14c) onto 14b) shows the maximum strength to be assigned a hydration product of a chemical composition lying in the blast furnace slag field (KS) in the triadic system $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$.

Finally, Fig. 14d) shows water contents of hydration products of hardened cements made with different lime hydrate dosages to monotonously decrease vs. $\text{Ca}(\text{OH})_2$ proportion. Hydrate products in the KS field contain about 5 mols of H_2O for each mol of SiO_2 .

This test was remade with artificial mixtures of silica gel, hydrargillite and lime hydrate, as well as with pumicite admixed with 25% of portland cement. Test results seen in Fig. 15 show these artificial mixtures to have the highest strength where composition of the hydration gel lies in the blast furnace slag field in the triadic system of chemical composition.

3. Conclusions

The observed hydraulic setting ability of mechanically activated natural pumicites admixed with hydrate, approximating that of medium-grade portland cements, has been attributed to the following concomitants to mechanical activation:

a) In course of mechanical dispersion by fine grinding, the specific surface of the system increases, at the same time capillaries and pores in the pumicite particles are disclosed.

Growth of the specific surface accelerates the chemical reaction with lime hydrate, just as any heterogeneous chemical reaction can be accelerated by increasing the dispersity degree of the system.

Disclosure of the capillary system in the particles is advantageous for lime hydrate reaction by erasing the water absorptivity of pumicite particles otherwise rather detrimental to the water balance of (hampering) the chemical reaction between silicate and lime hydrate.

The rate of chemical reaction between silicate and lime hydrate being crucial for the setting ability, in conformity with the above, simple fine grinding, that is, increasing the dispersity degree has to be considered as primordial for the increase of the setting ability of pumicite.

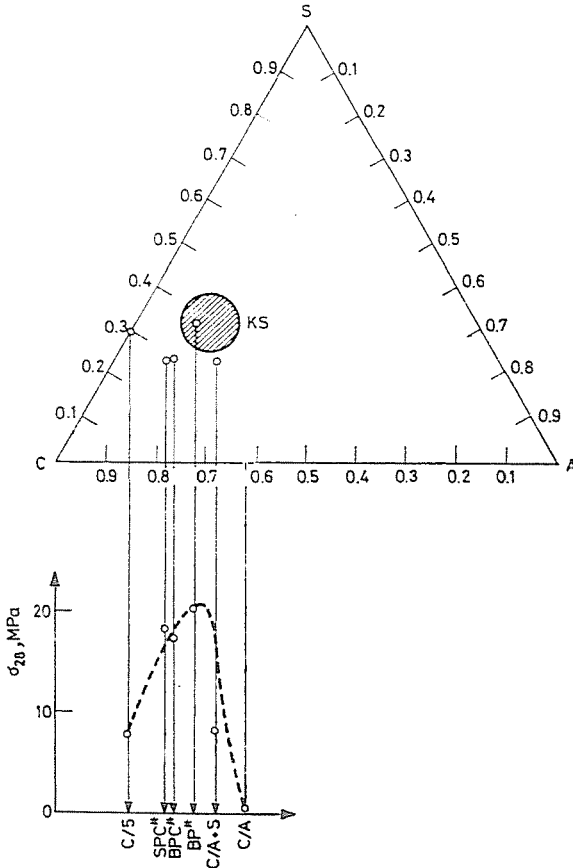


Fig. 15. Chemical composition and setting power of hydration products of artificial gel mixes and activated pumicite-lime hydrate-cement mixes

	C/S	C/A	C/A + S	SPC*	BPC*	BP*
Silica gel	34.2	—	29.7	—	—	—
Hydrargillite	—	49.0	14.1	—	—	—
Lime hydrate	65.8	51.0	56.2	23.0	23.0	30.0
Portland cement	—	—	—	23.0	23.0	—
Pumicite	—	—	—	54.0	54.0	—
W/C ratio	0.8	1.1	1.1	0.34	0.34	0.27

b) Especially surface activation concomitant to fine grinding elicits secondary processes harmful in themselves to the setting properties. These are *aggregation* and *agglomeration*, partly reducing the specific surface of the system, partly forming porous aggregates, and partly causing active surface centres to be covered by other particle surfaces (overlapping effect). These secondary mechano-chemical processes decelerate the chemical reaction between silicate and lime hydrate, impairing thereby the setting properties.

c) The possibility to increase the setting ability of pumicite more than the increase of the dispersity degree of the system can be attributed to mechano-chemical activation, feasible, in turn, by "supergrinding", of an intensity higher than that of fine grinding. Our tests unambiguously confirm the supposition of radical changes in the silicate structure upon mechanical effects.

These changes are the following:

- Release, then recovery, of water; — bound in the original pumicite structure by relatively high chemical forces — by the silicate structure of the grind (see changes of the depolarization degree and of the activation energy of water release).
- Release of cations bound to the silicate lattice in the vitreous structure of the original pumicite, and their transformation to amorphous oxides. The inner structure of particles in the supergrind may be considered as a molecular mix of amorphous oxides. The transformation can be quantified in terms of the variation of chemical reactivity, e.g. increase of the "Al-solubility".
- In the mechanically activated pumicite, cations — released from the vitreous steric net — are able to react with other materials e.g. lime hydrate, independent of each other. Thereby a calcium-silicate-aluminate-hydrate gel, of a composition optimum for hydraulic setting, can arise.

Thus, super-grinding, eliciting mechano-chemical activation, results in a quality change of the chemical properties of pumicite.

d) Approximate composition of silicate found to be optimum for hydraulic setting:



about corresponds to a silicate net containing four tetrahedral coordinations, among them three are of (SiO_4) and one is of (AlO_4) composition as an average; each double tetrahedral combination gets two Ca ions. Al substitution facilitates development of the steric structure, important, in turn, for the development of the setting ability. Mechano-chemical activation releases aluminium in a quantity needed for the reaction forming gel of the above composition from the vitreous structure of pumicite.

Summary

Tests have been made to determine the efficiency of mechanical activation of pumicites, aqueous volcanic glasses, — by supergrinding, of an intensity higher than that of normal grinding.

Test methods have been developed for determining mechanically induced changes in the glassy structure. These methods are: measuring oxygen compactness, dielectric constant and solubility, as well as chemical composition, X-ray and thermoanalytic curves, density, heat of solution and specific surface. Reactivity of activated materials with lime hydrate was concluded on by chemical methods and by testing the hydraulic setting of lime hydrate pastes.

The reaction of pumicite with lime hydrate was found to be much accelerated and intensified by a preliminary mechanical activation by means of supergrinding, achieving a setting ability equal to that of lower quality cements, attributed to the mechanical disclosure and grain size reduction of the originally porous pumicite particles, and mainly, to the destruction of the glassy silicate structure. These changes cause the formation — by chemical reaction with lime hydrate — of calcium-aluminium-silicate-hydrate gel, similar in composition to hydrate blast furnace slags, and its presence is fundamentally important for the development of high strength hydraulic-lime systems.

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