

Cementation of Soil Minerals with Portland Cement or Alkalis

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Although cementation of mineral surfaces has obvious importance in coarse-graded mixtures such as concrete, surface reactions become even more important in finer-grained mixtures such as soil-cement because of the far greater surface areas involved.

Unexpected long-term hardening of certain soil-cement mixtures has led to a hypothesis of hardening involving not only changes in the hydrating cement gel, but also changes within the surface layer of the mineral grains. The hypothesis follows Weyl's proposals of polarization or readjustment of ions near the surface of a solid to partly compensate for the unbalance in forces occurring at that surface. According to theory, such polarization "screening" should reduce the potential of a surface for chemisorption, or chemical bonding to other ions.

Once a mineral comes in close contact with an inorganic cementitious gel, bonds developing between the mineral surface and the gel should tend to reduce the unbalance in forces at the mineral surface. Because the cause of initial polarization is less, the polarization may reasonably be expected to become less. Reduced polarization then allows improved chemical bonding at the surface of the mineral, which in turn allows a further reduction in polarization screening. Thus a bond should show a gradual increase in strength over a period of time.

The data show a logarithmic relationship between compressive strength of soil-cement and curing time. Knowledge of the relative polarizability of various minerals may correlate with the rate of strength gain.

● **CEMENTATION CAN BE IMAGINED** as a combination of mechanical bonding of the cement to rough mineral surfaces, plus chemical bonds developing between the cement and the mineral surfaces. The latter process becomes more important as materials become finer grained; surfaces tend to be smoother, and more surface area is available. Portland cement stabilization of fine-grained soils thus emphasizes the chemical aspect, although answers obtained here would be expected to apply to a lesser extent in the cementation of coarse materials.

The present paper offers a hypothesis whose only pretense is perhaps to be reasonable in context, albeit rather evasive in proof.

BONDING IN MINERALS

Minerals are crystalline; that is, they have an orderly internal arrangement of atoms. The bonding between atoms is primarily ionic in character, though covalence, or electron sharing, does exist. Purely ionically bonded atoms retain their respective electrons and are attracted electrostatically because of the net plus and minus charges. These are not true bonds in the strict sense of the word, they are forces. Adjacent oppositely charged ions may be said to "screen" each other, since they act to balance out each other's forces.

Evidence shows that these two types of bonds (ionic and covalent) are transitional, and both can exist in any one linkage. Pauling (12) working with halides, developed

TABLE 1
ELECTRONEGATIVITIES OF ELEMENTS AFTER
PAULING (12)

Element	Electronegativity
H	2.1
C	2.5
O	3.5
Na	0.9
Mg	1.2
Al	1.5
Si	1.8
P	2.1
S	2.5
Cl	3.0
K	0.8
Ca	1.0
Fe	1.7

expressions relating the percentage of ionic character in a bond to the "electronegativity" of elements making up that bond. Electronegativity is the ability of atoms in a molecule to attract electrons. Electronegativities (Table 1) show a close relation to position of the element in the Periodic Table. A curve relating these to percent ionic character is presented in Figure 1. The greater the difference in electronegativity between two elements, the greater the percentage of ionic character existing in their bond.

A measure of ionic vs covalent bonding, as well as actual positions of atoms, is obtained by plotting electron densities from various crystal planes by techniques involving three-dimensional Fourier analysis of X-ray diffraction intensities. In an ionic crystal such as sodium chloride the electron density falls to zero between adjacent positive and negative ions. In a covalent crystal such as diamond the electron density between adjacent atoms does not fall so low (about 1.7 per cubic Angstrom in the case of diamond). In intermediate crystals the minimum electron density is intermediate (5).

For the most part the percentages of ionic character in various bonds occurring in minerals have not been measured, and one must rely on the relationship of Pauling (Fig. 1) to obtain average values. Calculated values important in minerals are as follows.¹

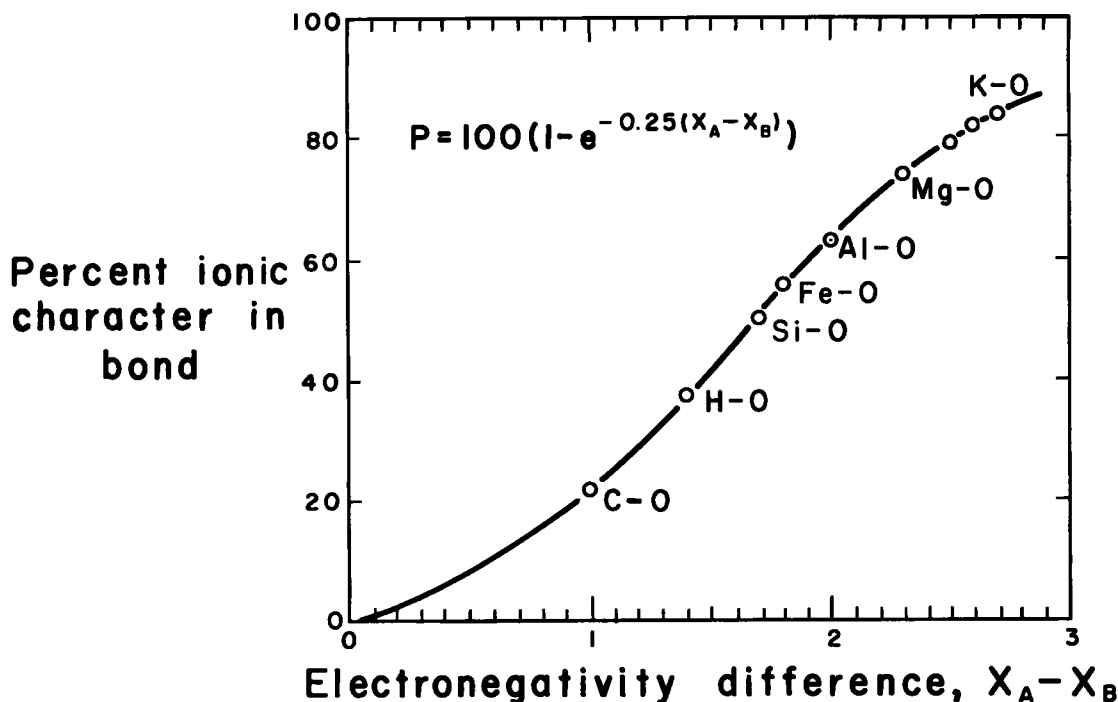


Figure 1. Percent ionic character in bonds. Calculated after Pauling (1).

¹ $P = 1 - e^{-1/4(X_A - X_B)^2} \cdot 100$. A modified treatment by Hannoy and Smyth, described in Coulson (2), gives $P = 16(X_A - X_B) + 3.5(X_A - X_B)^2$. Neither relationship is perfect because of difficulties in evaluating effects of resonance.

Of these only H-O and C-O are predominantly covalent in character. These occur as distinctive units in minerals, H-O as OH or in H₂O; C-O as CO₃ groups in the carbonate minerals. The Si-O bond is borderline.

So far the picture is relatively simple, and calculation of ionic character is uncomplicated if one anion and one cation combine to make up a molecule. But minerals often contain several kinds of cations, for example orthoclase feldspar, KAlSi₃O₈, and anions are usually shared by two or more cations. Gruner (6) in his application of Pauling's theories to mineral stability, simplified the problem by calculating the average electronegativity of all cations and adding a correction "bridging factor" for sharing of the O ions. Such a simplification is practical because in most minerals all cations are bonded to oxygen.

In discussing bond type, Pauling refers to "polarization," or electron shell deformation effects. Covalent bonds occur only when polarizability of the participant atoms allows the electron swarms to be distorted.

POLARIZATION AND SCREENING OF MINERAL SURFACES

Mineral grain interiors are essentially ions captured in a three-dimensional network of electrical forces. At a surface the continuity is interrupted and force patterns are disrupted. Surface tension is one result; the partial reorientation causes attractive forces to be diverted into the plane of the surface.

In a solid, several mechanisms may operate to reduce the energy in a surface. One of these, sorption of ions and molecules, is the goal of cementation. A second mechanism suggested by Weyl (16) is polarization of the surface ions, or distortion of their electron swarms. This is illustrated in Figure 2(b). Unbalanced forces are represented by arrows, and polarization tends to reduce the unbalance. Polarization is believed to be more pronounced in anions than in cations because of the larger diameter of electron swarms about anions. Thus polarization tends to create a negatively charged surface on a crystal. The extent to which polarization will take place varies depending on the nature of the ions and coordination of the bond. Large ions polarize more easily; small ions not at all.

A third process suggested by Weyl for reducing surface energy is distortion of the surface layer, the larger ions becoming slightly displaced and tending to "screen" the smaller cations. As seen in Figure 2(c), this would result in the formation of an electrical double layer in the surface of a mineral, the outer layer being negative. The difference from polarization is mainly one of degree, in that distortion in the surface layer also disturbs the force pattern of ions deeper in the crystal, and distortion screening effects probably extend a finite depth before dying out. The distortion mechanism may be analogous to the formation of an "amorphous" Beilby layer in metals.

A fourth mechanism important in stabilization of colloids is the formation of an electrical double layer by predominant adsorption of anions to screen the exposed cations. The process is here considered as part of chemisorption.

Comparison of Mechanisms

Polarization of surface ions. Of the above surface phenomena, polarization would be expected to take place on the crystal surfaces containing large ions having readily polarizable electron swarms. Polarization involving only the surface ions probably takes place rather quickly. Screening should be most effective when the number of cations can then be screened more easily. Polarization would presumably be decreased by covalent bonding tending to tighten the electron swarms around the affected ions.

TABLE 2

Bond	Percent ionic character
K - O	84
Na - O	82
Ca - O	79
Mg - O	73
Al - O	63
Fe - O	56
Si - O	51
H - O	39
C - O	22

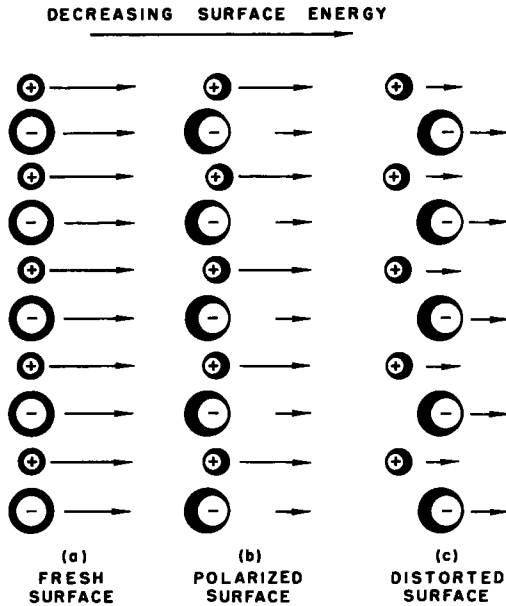


Figure 2. Polarization (b) and distortion screening (c) in a 100 NaCl surface. After Weyl (4).

Analysis of these factors suggests that silicates in general are only faintly polarizable in their surface layers.

Structural screening. The fact that surface ions are limited in their adjustment by the ions underneath does not mean that screening cannot occur; it means that ions underneath must move also. Eventually a surface zone of distortion may develop, each successive layer of ions being less out of place than the next one above. The sum of these distortions may add up to effective screening. X-ray diffraction of fine quartz powders reveals a strongly distorted zone extending 0.3 to 0.5 micron in from the surface. That these adjustments take time is evidenced by the fact that freshly ground quartz is chemically very active; it can lower the pH of water to below 5, presumably by adsorption of OH ions to cover unscreened Si^{+4} sites, and it can cause silicosis in man. The affinity of fresh quartz surfaces for anions is further indicated by presence of ozone in the grinding mill; O_2 covalent bonds are broken to supply oxygen ions and give a byproduct of $O + O_2 = O_3$ (16). Quartz

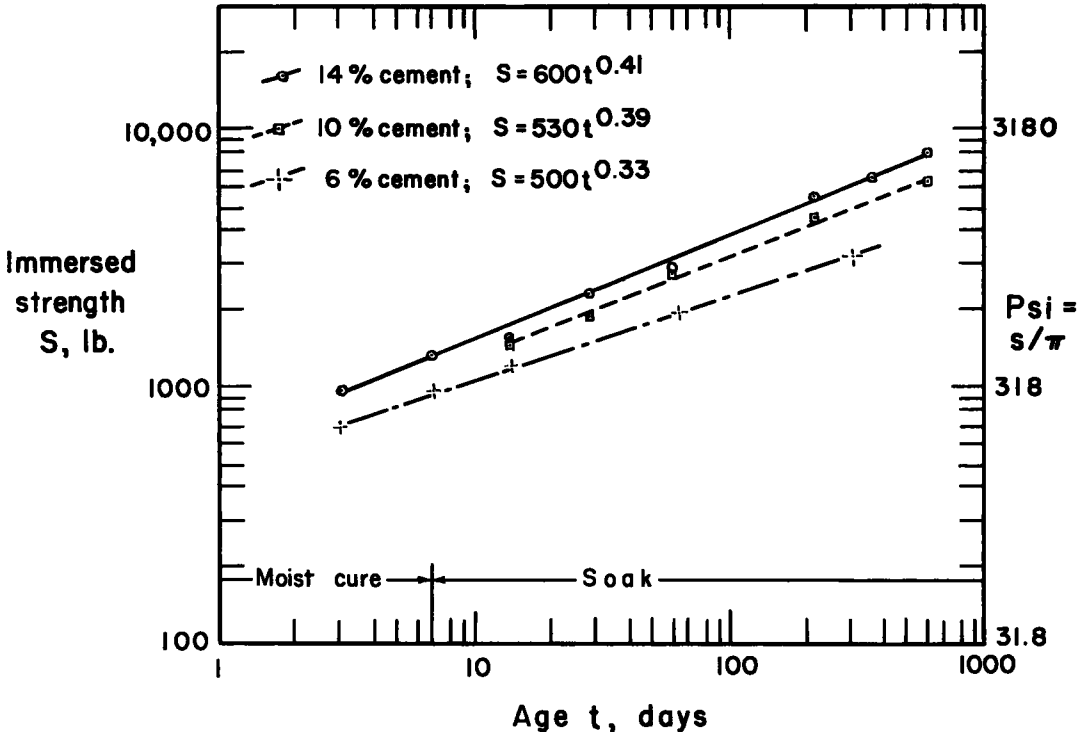


Figure 3. Relation between time and strength of 2-in. by 2-in. diameter soil-cement cylinders with Iowa loess sample 20-2. Samples were continuously soaked after initial 7 days moist curing.

which has aged a while is apparently less reactive and probably less dangerous.

For reasons discussed later, quartz probably has an unusually high amount of surface zone distortion, and it is interesting to note the relation between quartz weathering and particle size. Quartz with its screened surface is ordinarily rather resistant to weathering, more so than the feldspars, yet in the clay size range the relative positions of quartz and feldspar are reversed (9). Probably in fine particles the distortion effects fading in from one side of a crystal are met by similar effects trying to fade in from the other. The result is less effective screening and a surface more susceptible to attack.

Chemisorption. Adsorption of ions takes place to satisfy bonding energies unshielded by either polarization of surface ions or the deeper structural screening. Even mild chemisorption reduces the surface energy. For example, a polar liquid such as water will temporarily satisfy some of the surface forces and cause a reorientation, reducing surface tension and decreasing the scratch hardness of many silicate minerals. Thus quartz grinds more easily when wet with water, and glass scribes more easily if the cutter is wet with water. The adsorption of OH ions, by reducing surface tension of the quartz, also contributes to solubility. Quartz and silica glass are much more soluble in alkaline than in neutral or acid conditions.

ALKALI REACTIONS

Alkali reactions, now well documented in concrete (13), proceed most rapidly with amorphous or glassy materials such as opal, opaline chert, and volcanic ash. The reactions are not generally recognized as proceeding with quartz. This serves to emphasize an important point—a structurally-screened surface zone is not randomly constituted, as is a glass. The random bonding in a glass contributes to "weak places" which make the surface highly susceptible to attack. Screening distortions, on the other hand, increase the resistance to attack. Screening would also be expected to occur in a glass, reducing the suitability for reaction. But because of the disorganized internal structure, screening may not shield cations symmetrically, as in crystals.

CEMENTATION

Portland cement is an alkaline substance. Na_2O and K_2O are often present in minor amounts, the amount being limited to reduce alkali reactions with bad aggregates. $\text{Ca}(\text{OH})_2$ is released on hydration. Hydroxyl ions are thus available for immediate bonding to quartz. Polarization of the O ion may weaken the O-H bond and result in the loss of a hydrogen, but this is not known. Devore (4), in his application of Weyl's theories, considers OH ions to exchange for O ions in the surface of quartz, the displaced O ions being then bonded to the H. OH ions in this position are presumably more polarizable.

The picture is then $\begin{array}{c} | & | & | \\ -\text{Si}-\text{O}-\text{Si}- \\ | & | & | \end{array}$ distorted to $\begin{array}{c} & \text{O} & \text{Si} & \text{O} & \text{Si} & \text{O} \\ & | & | & | & | & | \\ & \text{O} & \text{Si} & \text{O} & \text{Si} & \text{O} \end{array}$ as oxygens move out. Adsorption

to complete the screening is either $\begin{array}{c} | & | \\ \text{Si} & \text{O} & \text{Si} & \text{O} \\ | & | & | & | \\ \text{H} & & \text{H} & \\ \text{O} & & \text{O} & \end{array}$ (Devore) or a direct adsorption of OH

onto partially covered Si, $\begin{array}{c} | & | \\ \text{Si} & \text{O} & \text{Si} \\ | & | & | \\ \text{OH} & & \text{OH} \end{array}$.

Devore develops his theory of hydration to show how a quartz surface might assume the configuration of a feldspar or mica, thereby increasing the probability of inter-growth with those minerals.

In his study of bonding with cement pastes, Munger (10, 11) suggests that cement gel develops spontaneously on a mineral surface, bonding to the exposed oxygens, growing by polymerization of the SiO_4 groups, and incorporating free calcium ions into the linked SiO_4 superstructure. Bonding thus depends on the number of surface oxygens either in the ionic or covalent state. Munger correlates early bond strength

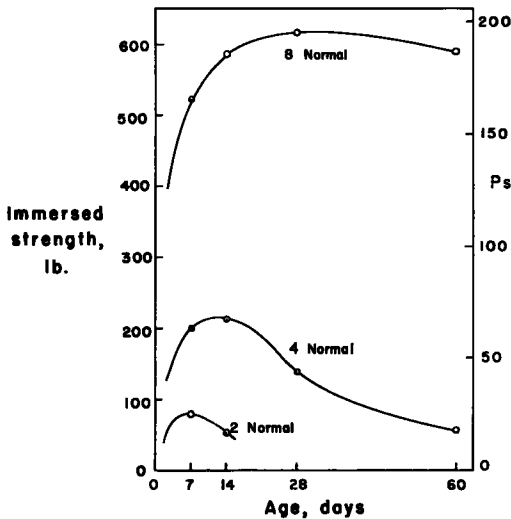


Figure 4. Strength of 2-in. by 2-in. diameter loess specimens compacted to standard Proctor and with various normality NaOH solutions substituted for added water (15 percent). Continuous moist cure, with 24 hour immersion prior to testing.

strengths reaching almost 3,000 psi (80). Furthermore the increase in slope (the exponent on t) between 6 and 10 percent cement is significant, whereas the change from 10 to 14 percent cement is rather small. This suggests that above a certain minimum content of cement the hardening is not dependent on changes in the gel but reflects increased bonding to the mineral crystals. If the gel alone were affected there should be a closer relationship between slope and cement content. Also, the failures appear to involve breaks from the grain surfaces, not breaks through the grains, as sometimes occurs in coarse aggregates in concrete.

It would appear that as cementation proceeds, screening by polarization and distortion may change. Development of new bonds on an ionic surface should logically cause an immediate reorganization of the force pattern, the amount of the reorganization depending on the strength and number of cementation bonds. The net effect should be to reduce the surface disruption that caused screening, and to cause structural adjustments which would increase cementation by providing a more satisfactory atomic surface pattern. Should a previous nonstoichiometric surface adsorption be involved, diffusion of cations through the cement gel could make up the valence deficiency. The increased bond strength might then cause a further change in screening, which would give a further boost to bond strength. Thus an interdependence may exist whose effect is to put a time lag in the strengthening of cementation bonds.

The time necessary for such hypothetical adjustments to take place is unknown. If the polarization effects were only "skin-deep" as in Figure 2b, adjustments should be almost immediate, since they involve only the surface electron swarms. On the other hand if screening involves distortions extending tens or hundreds of ions into a crystal, with distortion of each successive layer depending on unbalanced forces set up by distortions in the last, time may become important.

The time required for adjustments to improve cementation should be longer than the time for structural screening of a fresh surface. Original screening was caused by a sharp discontinuity at the surface, whereas the opposing forces of cementation are at first comparatively weak. Their weak force pattern must be mirrored by an adjust-

to the effective number of oxygen ions, and later bond strength to the degree of covalent bonding of oxygens. He believes covalent linkages strengthen as a result of the continuing polymerization.

Munger's theory would at first suggest that structural displacement screening would improve early cementation by increasing the exposed area of oxygen ions. On the other hand an unscreened or partially screened surface will immediately become coated by oxygens or OH ions from solution. Neither of these factors enter into Munger's calculation except indirectly, since both screening and effective ion calculations depend on kind and number of internal cations.

ADJUSTMENTS FOLLOWING CEMENTATION

The strength of soil-cement and concrete continues to gain through years, although data on mortars show that cement hydration has essentially stopped after about 24 months (2). Figure 3 shows the relationship between strength of a portland cement-stabilized silt and time, with

TABLE 3

TENSILE STRENGTHS OF MORTAR BRIQUETS IN PSI¹

Aggregate	Formula	52-hour moist cure	24-hour moist cure, 24-hour autoclave 150 C, broken at 52 hr		52-hour moist cure
			14 months soak	370	
Rose quartz	SiO ₂	92	515	340	} 370
Smoky quartz	SiO ₂	84	540	360	
Milky quartz	SiO ₂	85	575	410	
Microcline	KAlSi ₃ O ₈	90	105	450	
Plagioclase (Labradorite)	NaAlSi ₃ O ₈ + CaAl ₂ Si ₂ O ₈	111	210	405	
Marble	CaCO ₃	78	90	370	
Magnesite	MgCO ₃	155	585	730	

¹ Minerals constitute 1:4 by volume. After Thorvaldson (15).

ment in screening before a stronger pattern can develop. Thus the lag may be considerable. The long-term effect is a slow relaxation of screening and an increase in bond strength.

ACTIVATION

Heat. The previous discussions suggest that quartz, with its deep surface zone distortions, may be a bit slow at developing its potential cementation bond strength. One way to hasten readjustments in the surface zone may be by use of heat. Data by Thorvaldson (15) in Table 3 show a high strength gain of quartz mortars after autoclaving at 150 C. The same is true for mortars made with quartzite, flint, or chert, and for mortars made with highly quartz-bearing igneous rocks. In his closure to this paper Thorvaldson mentions that lime and quartz become reactive at 150 C and new reaction products are formed. With normal temperature curing the full strength apparently is not fully developed after 14 months. Thorvaldson uses these strengths as a standard for the comparison of mortars made with other minerals.

Alkali. The solubility of quartz in alkalis suggests a solution for the troublesome surface layer—namely, solution of part of the troublesome surface layer. Treatment of loess with a solution of NaOH alone gave considerable strength, probably by incorporation of the surface layer of quartz into a gel which would borrow exchangeable calcium from the clay. Note that strengths came only at early ages (Fig. 4) and there is no latent strength gain as from reorganization within the mineral surface layers.

Treatment with strong alkali should improve the reactions of quartz with alkaline stabilizers such as lime or portland cement. Unpublished research shows early strengths may be raised 15 to 400 percent by use of strong alkalis. Anderson (1) attempted to correlate petrographic data with alkali reactivity of Iowa loess, and while the correlation with quartz surface area is imperfect, as shown in Figure 5, there does appear to be a relationship. The other major minerals in loess are feldspars and carbonates, discussed below. The equation for Reactivity Index is from earlier work by Handy, Davidson and Chu (8).

RELATIONS TO KINDS OF MINERALS

Feldspars and quartz. Quartz is about 50 percent ionically bonded and comparatively well screened by distortion in the surface layer. Feldspars, which are tectosilicates built on a three-dimensional framework as is quartz, contain Al⁺³ substituted for some of the Si⁺⁴, the valence deficiency then being made up by Na⁺, or Ca⁺⁺: The result is a preferred directional bonding leading to cleavage, and a net increase in the number

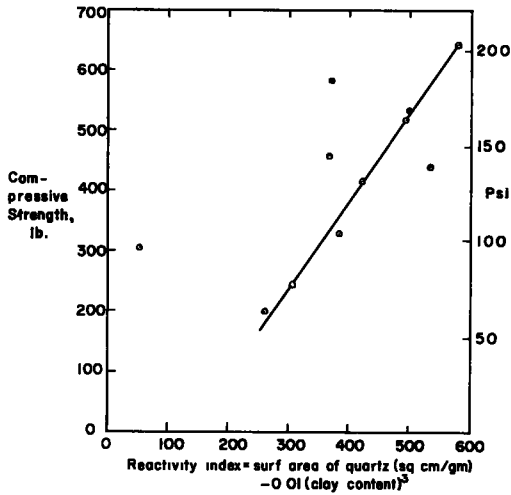


Figure 5. Compressive strength of 8N NaOH-treated 2-in. by 2-in. cylinders molded with various loess samples. Quartz surface area measured microscopically on material coarser than 5 microns.

probably less pronounced in feldspars because of the lower surface energy to start with, better polarization of the surface layer, and lower average valence on the cations, amounting to a deconcentration of charge. From this analysis one would expect (a) moderate early cementation bond strength, less than the potential in quartz because of the reduced but asymmetrical covalent bonding, (b) no special reactivity at high temperatures, (c) a long-term strength gain unrelated to relaxation of distortion screening, and (d) no benefit from dissolution of the surface layer other than to clean the grains.

Carbonates. Calcite, CaCO_3 , is another step in the same direction as feldspars. Calcite contains covalent CO_3 groups occurring in planes and bonded to one another by ionic O-Ca-O bonds. Because of polarization of the oxygen ions bonded to C, the Ca-O bonds are rather weak. Therefore calcite is softer and more soluble than most silicates. It also has very good cleavage. Screening at a surface would be expected to be nil. Therefore cementation bond strength should develop rapidly and show little high temperature improvement (Table 3). From the standpoint of removing screened zones there should be little advantage in chemical treatment. High long-term strengths (Table 3) are unexplained but are believed unrelated to screening.

Magnesite, MgCO_3 , was found by Thorvaldson (15) to be peculiarly reactive on autoclaving, whether incorporated in mortar as a pure mineral or in the rock dolomite, $\text{MgCa}(\text{CO}_3)_2$. He suggests that the solubility may be a factor. $\text{Mg}(\text{OH})_2$ is less soluble than MgCO_3 , resulting in dissolution of the carbonate and precipitation of the hydroxide, probably as brucite. Highest strength was found after long curing (Table 3).

Clay minerals. Clay minerals and micas are platy crystals classified as phyllosilicates. Weyl (16) believes that clay flakes are so thin (7-10A) as to prevent satisfactory structural screening, and he attributes the electrical effects observed on clay to this cause. Adsorption of OH ions on the unscreened sites would serve to make the clays negative. However, isomorphous substitutions add to negativity of many clay minerals.

Cations within the clay mineral are automatically partly screened by their positions in tetrahedral and octahedral layers. Three-layer clays such as illite have predominantly O^{--} ions in their surfaces, whereas two layer minerals such as kaolinite contain both

of cations and in the ionic character of the bonding. The existence of inherent cleavage directions signifies a relatively lower surface energy along those planes; less energy is required to make a new surface. Cleavage probably takes place because of the comparatively weaker ionic bonding, especially since the nearby Si-O bonds may be strengthened by unsymmetrical polarization of the oxygen ions, giving a better Si-O covalent bond (14). It should be pointed out that in general the most stable silicate minerals are those with the most covalence.

The surface of a feldspar would be expected to contain metallic cations screened by polarization, especially since the cations, particularly potassium, are somewhat polarizable themselves.² Polarization of the surface ions should offer little hindrance to cementation compared with the deeper more lasting distortions found in quartz. Such structural adjustments are

² The radius of Na^+ and Ca^{++} ions is about 1Å; that of K is about 1.33Å. Larger ions are the more polarizable. For comparison the radius of O is 1.4Å. Si^{++} , on the other hand, has a radius of only 0.4Å. Al^{++} has a radius of 0.5Å. Figures are from Lange, Handbook of Chemistry, 8th ed. (1952).

TABLE 4

UNCONFINED COMPRESSIVE STRENGTHS OF COMPACTED LIME-FLYASH MIXTURES. 92% FLYASH, 8% LIME (17).

Flyash	Loss on ignition	Compressive strength, psi			
		20 C cure		60 C cure	
No.		7 days	45 days	7 days	45 days
10	3%	240	2250	2250	2700
11	28%	40	190	420	570
12	10%	50	950	1200	1550
15	17%	120	900	1100	1250

O^{--} and OH^- . The average bond type within the crystal approximates that of quartz or feldspars³, but this may be of little direct importance because of the variety of bonds occurring. The exceptionally good cleavage representing weak surface forces would be a barrier to bonding, more so than in feldspars and calcite, and there would be no surface adjustments to give slow improvement. This disregards hydration and the flocculation by excess calcium from the cement. Flocculation takes place quickly but is a comparatively weak bond. Probably more important are long-term chemical changes within the clay minerals brought on as a result of the change in the environment. Clay minerals are uniquely susceptible to such modification.

Amorphous materials. Glasses deserve close attention because of their usefulness as pozzolans. Natural glasses and flyash vary considerably in composition, but are essentially mixtures of Al_2O_3 , SiO_2 , and Fe_2O_3 , plus lesser amounts of other oxides. The bonding is therefore mainly ionic and probably variable according to localized coordination conditions. As already discussed, screening probably occurs but is imperfect because of randomness of the inner structure. However, one would expect the reactivity of pozzolans to be particularly enhanced by alkalis or by heat because this would expose disorganized glass. The effect of heat on curing of flyash, an artificial pozzolan, is shown in Table 4. Benefits would be expected to be greatest in pozzolans highest in silica, as the higher valence on silicon means fewer cations to be screened than if the cations are Al^{+3} or Fe^{+3} . In the case of flyash, the composition varies so much from grain to grain that almost any flyash should be benefited—each grain

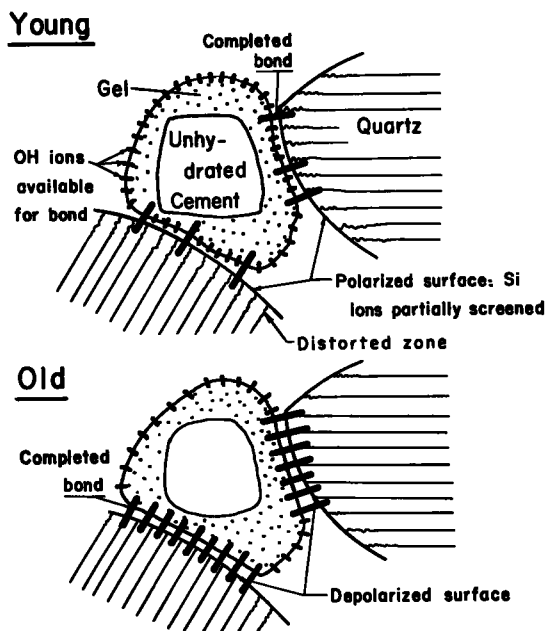


Figure 6. Diagrammatic representation of a theory of cementation. Early cementation bonding is weak due to distortion polarization of the quartz surface. However, the early chemical bonding causes distortion to slowly disappear. This in turn allows even greater chemical bonding.

³ Using Pauling's relationship and electronegativities from Table 1, Orthoclase, $KAlSi_3O_8$, gives $X_B = (0.8 + 1.5 + 3 \times 1.8) / 5 = 1.54$. Kaolinite, $Al_2O_3 \cdot SiO_2 \cdot 2H_2O$ gives $X_B = (2 \times 1.5 + 1.8 + 2 \times 2.1) / 5 = 1.8$. Muscovite, $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$ gives $X_B = (2 \times 0.8 + 6 \times 1.5 + 6 \times 1.8 + 4 \times 2.1) / 18 = 1.66$.

of flyash represents the composition of a parent mineral grain in coal; there is very little combination and averaging of the product during burning.

SUMMARY

A hypothesis is advanced to explain long-term strength gains in soil-cement by readjustments within the mineral surface, tending to improve chemical bonding. The hypothesis is extended to pozzolans and representative minerals in soils and in concrete, and offers an explanation of activation of silica by heat and by alkalis.

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