The Pessimum Proportion as a Reference Point in Modulating Alkali-Silica Reaction[1]

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Six varieties of chert from a single limestone formation (Dev. Onondaga) of central and western New York were investigated with regard to their alkali reactivity and how that reactivity might be related to geological factors of their origin and petrology.

The cherts consist predominantly of microcrystalline quartz with minor, but varying, amounts of cryptocrystalline quartz, chalcedony, megaquartz (vug filling, or other authigenic quartz), quartzite (equant grains with strongly interlocking and sutured contacts) and trace amounts, in one of the six cherts in the study, of isotropic silica, probably opal.

To prepare material for mortar-bar and "quick-chemical" testing the cherts were broken out of the limestone matrix, and the most homogeneous and purest portions selected for cleaning with abrasive wheels to remove all adhering limestone.

The six cherts were combined in six concentrations (5, 10, 20, 50, 75, and 100% of the total aggregate) with rose quartz, the diluent or control aggregate, for the Mortar-Bar test, ASTM C 227. The cement used for fabricating the mortar-bars was Type I, with .89% alkalies by laboratory determination. The nominal alkali content as given by the supplier was 1.06%.

The results of the quick chemical and mortar-bar tests are summarize in Table 1, and Figures 1 and 2.

With reference to Figure 1, as has been evidenced in numerous studie there is a certain concentration, or proportion of reactive to control aggregate, which displays the maximum expansion - the pessimum proportion.

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It is observed that at what are distinct ratios of concentrations of available alkalies to reactive aggregate, symmetrically on either side of the pessimum proportion, the expansion, e. g. at the extremes, is notably lower than that of the pessimum bar. Work has been reported wherein it is shown that large, or superfluous, amounts of alkalies suppress or inhibit expansion of mortar-bars containing what would otherwise be very expansion-causing aggregate. Similarly one might observe that large or superfluous amounts of reactive aggregate, relative to a given concentration of alkalies, are not right to obtain the most expansive proportion. Percent expansion seems in some cases to be quite symmetrical about the pessimum, suggesting similar reaction rates and that the product of certain quantities at concentrations equidistant from the pessimum is equal to a constant.

Regarding the end point conditions which are intuitively more clear cut and unambiguous, one can hypothesize that in one case the ratio alkalies/reactive aggregate is either too small, i. e. too much alkalies for the available chert, or too large, too much chert for the available alkalies, to maximize expansion. What those limiting conditions are, and where the pessimum proportion will lie, is a function of the particular petrographic character of each chert which in turn controls its rate of reaction and the efficiency of utilization of the available alkalies.

If the expansion is, in the final analysis, a function of the ratio of available alkalies to reactive aggregates, it is tempting to speculate -- for actual construction practice where high alkali cements and reactive aggregates might or could be used -- that by manipulation of concentrations of alkalies and reactive aggregate one might achieve the more benign ratios of alkalies to reactive aggregate that exist at certain distances on either side of the pessimum proportion.

However, present understanding of the pessimum proportion is largely empirical and qualitative, and approaches which suggest the combination of deleterious materials in ways and amounts which might be regarded as imprudent, in the absence of a systematic understanding of the phenomena, would be contrary to good engineering practice. That is, if the proposed combinations of materials were regarded as speculative, and not sufficiently rationalized, because they were based on empirical understanding, they could be considered to be leaving too much to chance to suit pragmatic engineering decisions.

Mielenz (1947) has suggested that the pessimum proportion represents the operation of two opposing characteristics of cement aggregate reaction, namely: the tendency for increased expansion as progressively more reactive particles are made available for attack and the tendency for decrease in the silica-producing reaction as the available alkalies are more and more

rapidly depleted by absorption and liberation of silica over the greater and greater surface area exposed to attack.

It would seem sensible that the amount of expansion, in an all other things being equal situation, is some function of the amount of alkali-silica gel produced. If so, we can recast the foregoing idea as a starting place for a more rigorous representation of the reason for maximum expansion at a given concentration of reactive constituent.

The two concurrent, but opposing, characteristics of the reaction are the tendency for increased expansion as more and more of the product causing the expansion is produced as a consequence of increase in amount of one of the reactants, the available silica. At the same time there is a depletion in the amount, or potency, or effective concentration of the other reactant, the available alkalies, as a consequence of the increase in amount of the first reactant.

The amount of reactive surface increases directly with the concentration of reactive aggregate and at the same time the amount of alkali is spread over or depleted proportional to the same rate of increase of the available reactive surface, i. e. twice the amount of surface area is available at e. g. 40% concentration of reactive than is available at 20. Therefore, sensibly, whatever is the nature and amount of association of alkalies with reactive surface that occurs at 20%, twice as much of it occ at 40%. Or, alternatively, is some other, but still systematic, function percent reactive constituent.

The amount of expansion that results is proportional to the amount o reaction product formed but this is in turn proportional to the amount of surface available and the effective alkali concentration relative to that surface, and that quantity is continually decreasing as the amount of surf increases.

This relation can be depicted numerically and graphically by the following illustration. Consider a set of mortar-bars in which the percer of reactive constituent is varied from zero to 100%, the alkali content of the cement used is 1%. A reaction proceeds in which a certain amount of alkali, proportional to the amount of reactive constituent, is removed fro the paste by virtue of its combination with the reactive constituent. The balance of the alkali remaining in the paste, proper, is now different in each mortar-bar, higher in the bars with low reactive aggregate and decreasing as the percent reactive aggregate increases. If the amount of expansion that occurs is taken to be proportional to the interaction at any stage of the process between the amount of initial reaction product formed and the balance of the alkalies remaining in the paste we can generate a model that may fairly represent the occurrence of a pessimum proportion (Figure 3a).

A- 1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0
B- 0	10, (.1)	20, (.2)	30, (.3)	40, (.4)	50, (.5)	60, (.6)	70, (.7)	80, (.8)	90, (.9)	100
C- 0	.09	.16	.21	.24	.25	.24	.21	.16	.09	0

Line A represents the balance, or concentration, of alkalies remaining in each mortar-bar after an "initial" depletion which was proportional to the amount of reactive constituent present. Depletion rate in this case is one percent alkalies per percent increase in reactive constituent.

Line B is the percent reactive constituent with an amount of alkalies ( ) combined with it, which amount is proportional to the amount of reactive constituent and reaction product.

Line C is the value of A multiplied by the corresponding value of (B), it is a number proportional to the percent expansion, and represents the interaction between the amount of reaction product formed, proportional in each case to the amount of reactive constituent, and the remainder of the alkalies in the paste, whose concentration, or amount, is proportional to the values in line A.

If the values of line C are plotted vs. the concentration of reactive constituent the relation is as shown in the graph (Figure 3a) and it is seen that expansion decreases on either side of the 50% pessimum proportion. A more formal development of this proposition is given in attachment 1, and is based on the idea that the sum of the bound and remaining alkali is constant.

In the illustration chosen the rate of alkali depletion is such that at 100% reactive constituent the available alkalies are totally depleted. This is, for this illustration, the limiting condition which the process approaches. But at any stage, in the process of alkalies reacting with aggregate, the amount of alkali that will have combined will always be proportional to the amount of aggregate.

Similarly, as the process of alkalies combining with reactive constituent proceeds, although it may have been slow or fast, depending on the type of reactive aggregate and the alkali concentration, a point is reached, and passed, where a given percent of the reactive constituents will have combined with as much alkali as it is capable of, according to its available surface area. And, it is suggested that the relative expansions are, at any stage, proportional to the product of this quantity, the combined or bound

alkalies, which is in effect a concentration, i. e. units of alkali/ unit of reactive surface, and the concentration of the balance of the alkalies in the paste. Further, the concentration of the bound alkali to, or on the surface of, the reactive constituent is, on a unit basis, exactly the same for all concentrations of reactive constituent, e. g. , .1/10 =.2/20, etc., at, and at all stages prior to, the saturated or fully found surface condition. Let us assume a saturated, or fully found, surface condition with amounts of alkalies remaining in the paste and combined with the reactive aggregate respectively, as given in lines B and C. We now have a condition, along line B, in which the percent of reactive aggregate increases but the unit concentration of alkali to that reactive aggregate is the same. At the same time, each concentration of reactive aggregate is paired, in each mortar bar, with an amount of uncombined alkali which, in each case, is different. One of these amounts, or concentrations, of alkali remaining in the paste (1. 0, 0. 9, 0. 8, etc.) when paired with the fixed, or constant, concentration of alkali per unit area of reactive aggregate is more conducive than the others to optimizing the process which causes expansion. It is suggested that that concentration will be one which gives the proportion of 1:1 between the bound and remaining alkalies. In the particular illustration given, in which the pessimum is 50%, it is at that concentration at which half the alkalies remain in the paste and half are associated with the reactive aggregate. For lower concentration of reactive constituent the ratio of remaining, to combined alkalies is > 1 and for higher concentrations is < 1. It is suggested that as reaction proceeds from the beginning or from this stage, and as the alkali associated with the reactive aggregate further interacts with the alkali remaining in the paste, the optimum gel chemistry for expansion, i. e. the optimum ratio of alkalies to silica is produced earliest in that mortar-bar containing that concentration of reactive constituent which first achieves the 1:1 ratio of bound to remaining alkalies.

Pessimum proportions obviously do not, and need not all occur at 50%; it is evident that according to the above described mechanism the pessimum will occur at that concentration of reactive constituent which will have the <u>median</u> amount of depleted (or bound) alkalies[*]. Consider a reactive aggregate with a higher rate of removal of alkalies than in the first illustration. Each <u>unit</u> increase in reactive constituent removes an additional 1/10 of the starting concentration. Consider that the starting percent alkali concentration in the cement is again 1% but that by 5% concentration of reactive aggregate, the original 1% has been reduced to . 5%. We now have a situation as depicted in the following tabulation and Figure 3b.

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[*]And, which will at the fully bound or saturated point have depleted 1/2 the alkalies. Further, it will be the first concentration, from left to right, that will have the capacity to do so.

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A- 1.0  .9   .8   .7   .6   .5   .4   .3   .2   .1   .09    .08     .07     .06.....01 → 0.0

B- 0    1(.1) 2(.2) 3(.3) 4(.4) 5(.5) 6(.6) 7(.7) 8(.8) 9(.9) 10(.91) 11(.92) 12(.93).. 20... 30.. etc... 100

C- 0    .09  .16  .21  .24  .25  .24  .21  .16  .09  .082   .074    .065... etc. → 0% expansion
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Note that as the series proceeds to concentrations of reactive constituent greater than 5% it is, in a sense, necessary to deplete or distribute the remaining .5% alkalies over the remaining 95% of the reactive constituent. It would seem sensible that the initial rate of removal should continue up to the point (between 9 and 10% of reactive constituent) past which it can no longer do so. That is, after the ninth unit increase in reactive constituent, the capacity for depletion of the 10% of reactive constituent in the mortar bar(s) containing that and increasingly higher concentrations is so great, that essentially no alkalies remain in the paste. This is represented approximately by showing the remaining alkali for concentrations of 10% and greater gradually approaching zero as the concentration of reactive constituent approaches 100%. Similarly, line C, the series of numbers proportional to percent expansion approach zero as concentration approaches 100%.

A set of numbers corresponding to a pessimum proportion of 100% -- 100% of reactive constituent does not have the removal capacity to deplete the initial alkali content by one-half -- can be generated by any depletion rate of less than one percent of the starting alkali concentration per percent increase in reactive constituent. See Figure 3c.

If the foregoing explanation fairly represents the reason for the occurrence of pessimum proportions at various concentrations of reactive aggregate it suggests that where the use of potentially reactive aggregates and high alkali cements are contemplated it may be worthwhile to perform sufficient testing to determine what the pessimum proportion is, and what percent expansion is associated with it for a reference alkali content. It may be possible to realize economies in the use of materials without great sacrifice towards increasing expansion.

It is useful to know in which direction the pessimum proportion lies for a given alkali content and given percent of reactive constituent in the aggregate contemplated for use, since a limiting factor on expansion to the left of the pessimum is the availability of reactive constituent, while to the right it is the availability of alkali.

Also, it would appear that for concentrations increasingly further to the left of the pessimum, the less the relative penalty in increased expansion for increasing alkali content, and oppositely for concentrations to the right of the pessimum.

In a certain situation it might be found that the pessimum proportion is 60% and its degree of expansion is considered to be deleterious. However, the concentration of the reactive constituent in the deposit is 30% and its level of expansion is considered to be tolerable. A higher alkali cement can be used with the 30% since it will have the relative effect of driving the reaction down the expansion curve. In contrast, should the percent reactive constituent in the deposit be 70% but at a tolerable level of expansion, one is prepared with the information that the use of a higher alkali cement at 70% is likely to drive the reaction up the expansion curve.

Alternatively, one can reason that one should not practice dilution of reactive aggregate, out of fear, indiscriminantly without knowing wher the pessimum proportion for that aggregate lies. By not diluting far enough, or by diluting too far, the pessimum proportion might be achieve inadvertently.

It is difficult to argue that by adding alkali to, for example, a 40% reactive concentration, from a suite in which the pessimum is 60%, that the final expansion will be much reduced absolutely. It might not make too much difference, and at still lower concentrations the less difference it will make. But, adding alkali to proportions left of the pessimum may be a way of using higher alkali cement with certainly less potential penalty than using higher alkali on the right side of the pessimum.

Since addition of alkali will have the effect of shifting the pessimum to the right; compromising with expansion if it is added to a proportion left of the pessimum; increasing expansion if it is added to a proportion on the right of the pessimum, the most straightforward benefit is derived from working with percent of reactive constituent relative to the pessimum.

The preceding discussion although dealing with characteristics
of alkali silica reaction of a general nature was based on an investigation
in which the reactive rocks in question were quartzose cherts. In view
of renewed interest in alkali-silica reaction and especially involving
types of silica thought by many to be "stable" or non-reactive, or incapable
of deleterious degrees of reaction, the following remarks about the pro-
pensity for reaction of quartzose cherts and, by extension, of other quart-
zose rocks are offered.

Many investigators hold the viewpoint that the mineral quartz, the
thermodynamically stable form of silica at ordinary temperatures and
pressures does not participate in alkali silica reactions. Or, does not
participate if it is "well-crystallized" and unstrained. There seems to
be little disagreement that glassy and amorphous varieties, especially
opal, are reactive. The principal underlying reason for this being that
they dissolve much more readily in water, and esp. alkaline water than
quartz. Thr reason that they dissolve faster is that they are non-crystal-
line but it is the process of their being dissolved which leads to the form-
ation of sufficient quantities of silica gel to cause deleterious expansion.

Therefore, it would appear that the important consideration is not
crystallinity or thermodynamic stability per se but the extent to which
that, and other factors, increase the solubility of the silica in question,
whether the silica is in quartz, chert, opal, glass, etc.

Aside from the well known greater solubility of the noncrystalline
form of something relative to its crystalline form some other factors
which can increase the solubility of both forms are: the surface area over
which the solvent acts on the solute, the porosity and permeability of the
substance (but, rigorously considered, this eventually relates back to the
question of surface area), the presence in the solute of inclusions of water,
or of the solvent which is acting from the outside (again, this can be re-
lated back to increase of surface area), the presence of intrinsic strain
in the material, or, alternatively, strain induced in the material by
stresses acting in or on the system. (Intrinsic strain in rocks might be
of the residual kind resulting from geological stresses or, in natural
glasses, resulting from the material being part way along in the process
of devitrification. Induced strain might be caused by stresses which act on
the materials in all sorts of constructions - portland cement concrete in-
cluded.)

It is suggested that questions of degree rather than kind are involved in the distinction between reactive and non-reactive varieties of silica. A state of very fine aggregation, i.e., large internal surface area, the presence of micropores, water, and strain, aid and abet the reactivity of quartzose rocks greatly. So much that that fact may obscure the appreciation that, in terms of what is known about the crystal chemistry and chemical behavior of quartz, there is nothing to contradict the notion that quartz, by itself, without benefit of large surface area, strain, inclusions, and so forth, is very slightly and very slowly alkali reactive.

The solubility of amorphous silica (into which category opaline and glassy rocks may reasonably be placed) in water and its rapid increase in solubility with pH are known (Krauskopf, 1959) and have been commented on in the literature with respect to their obvious bearing on alkali-reactivity.

However, it is reported in more recent discussions by Krauskopf (1967) and by Smith (1963) that quartz has a definite solubility (10-15 ppm) in neutral solutions, and that solubility also increases very abruptly at about pH 9. If the curve shown in Krauskopf (1967), which more or less summarizes the data in Smith, is correct, the solubility of quartz at all pH's is within a factor of 10 of the solubility of amorphous silica, Figure At high pH's, ~> 11 the solubility of both forms is considerable and, it would seem, at still higher pH's and greater solubilities, the less important a distinction the factor of ten becomes.

In view of this it may be incorrect to conclude that the reactivity of all cherts and other quartzose rocks which have participated in alkali-silica reactions must, ipso facto, mean that some, or all, of the silica of which they are composed is opaline, non-crystalline, unstable, or strained, and that that material is responsible for the observed reactivity.

The cherts investigated in this study consist mineralogically essentia of quartz. It cannot be stated with absolute certainty that there is no opal other "amorphous" silica present whatsoever. Their presence would not l detected by X-ray diffraction and small, i.e. interstitial, amounts could b missed in petrographic examination. However, if these substances are present their volumetric amounts must be very small indeed - perhaps les than 1% of all of the chert sample from which the mortar-bars in this stud were fabricated. I am inclined to attribute the effects that were observed to those substances which I know to be present, rather than to those which might be inferred to be present.

Since chalcedony - at one time, but no longer, thought to contain interstitial opal - has been shown to consist of minute crystals of quartz with large numbers of micropores, it too is mineralogically essentially the same as the other more obviously quartzose substances. It follows in turn that the reactivity is attributed to the microcrystalline and cryptocrystalline quartz of which the cherts are dominantly composed.

It is suggested that the lack of deleterious degree of expansion of ordinary quartz can be reconciled with the deleterious expansion of quartzose cherts in this study, and in other studies, by considering that the (internal) surface area available for reaction of the cherts is enormous in comparison to that available from particles of quartz of the same size. And, that the deleterious reactivity of quartzose cherts is due to the intrinsic slight (but increasing markedly at pH > 9) solubility of quartz, producing slight gel formation with attendant slight capacity for expansion, which is increased, many fold, by the greater surface area available for reaction of the chert.

Midgely (1951) supplies the following data for the internal surface areas (in cm^2/gm) of materials similar to those under discussion: Chalcedony, 4,300; Flint, 2,200; Opal,. 400,000; Quartz, 0. Since opal and chalcedony are specifically mentioned separately it is reasonable to assume that Midgely's "flint" refers to a rock composed essentially of microcrystalline and/or cryptocrystalline quartz. It follows that the internal surface areas of the cherts studied in this investigation might be in the neighborhood of 2,000 to 4,000 cm^2/gm.

Quartz can produce a mortar-bar expansion of about . 033% at 12 months (Mielenz et al., 1947). This is about 15% of the maximum expansion caused by a chert in this study, and is one-third of the degree of expansion necessary to class a substance as deleterious. Thus, the quartz lacks being classed as a deleterious material by a factor of about 3, but if the same quartz were spread over a surface comparable to the internal areas of the substances reported by Midgely, its available surface area for solution and gel formation would be increased by a factor of thousands. Therefore, it would seem that its capacity for causing expansion, however that may precisely relate to increase in surface area, would be increased by an amount at least sufficient to account for the expansions observed in this investigation of cherts.

It is suggested that if this is the correct explanation for the expansion of quartzose cherts, i. e. , it being a phenomenon due almost entirely to their large internal surface areas, then the extension of the reasoning to other quartzose or siliceous rocks may be helpful.

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TABLE I

QUICK CHEMICAL AND MORTAR BAR TEST RESULTS
(IN ORDER OF INCREASING Sc/Rc)

Sample Identification	Alkalinity Reduction (Rc)	Dissolved Silica (Sc)	Sc/Rc	% Expansion Max. Mortar B.	Pessimum Proportion
55	111	312	2. 81	. 105	50%
45	174	504	2. 90	. 055	10%
44	95	312	3. 28	. 215	50%
73	106	353	3. 33	. 190	50%
57B	141	482	3. 42	. 200	20%
57	90	347	3. 86	. 225	50%

PERCENT EXPANSION VS. PERCENT CHERT: ELEVEN MONTHS
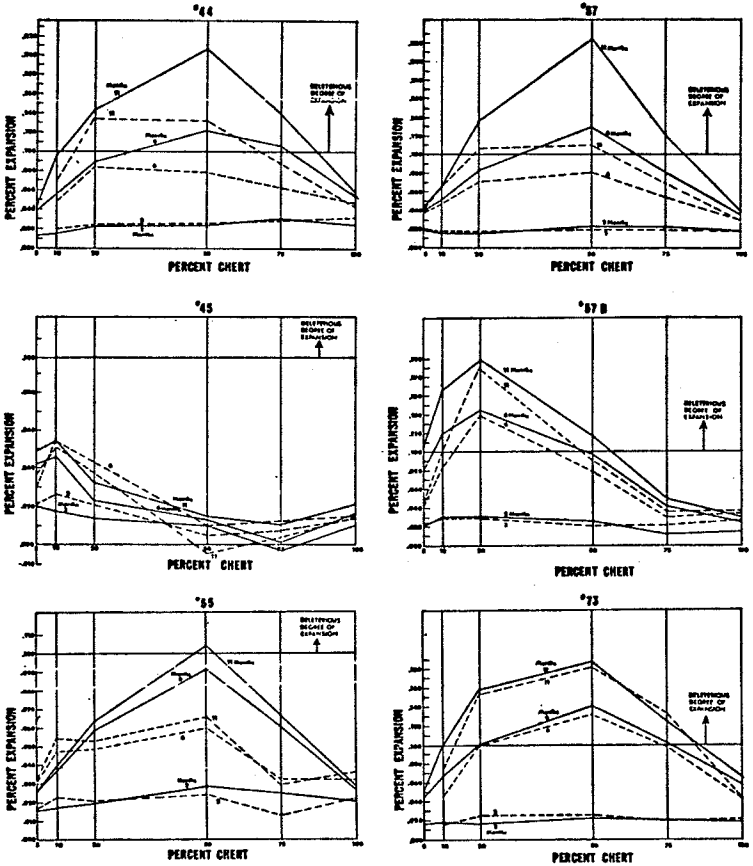
(Deleterious Degree of Expansion is . 10%)
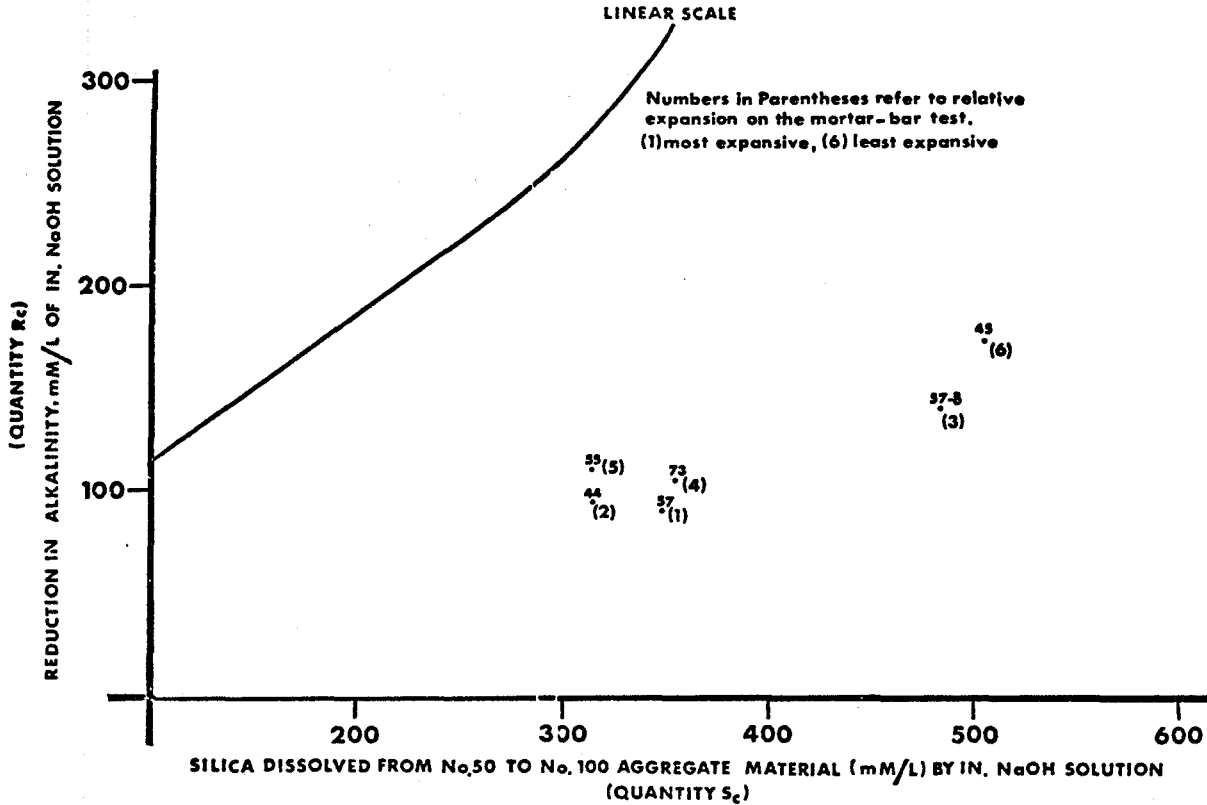
FIGURE 1

Figure 2. Relation Between Relative Mortar-Bar Expansion and Position on the
Quick Chemical Test Plot.

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Figure 3
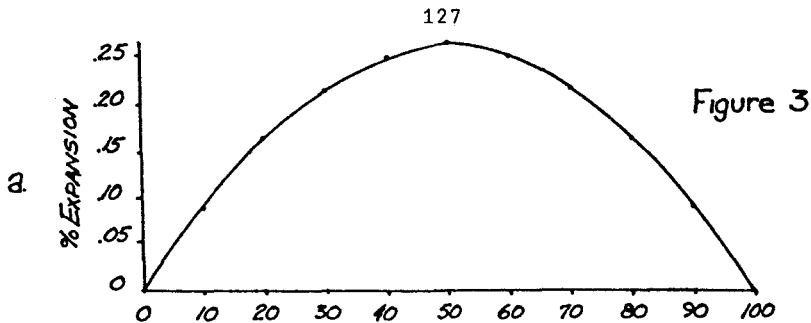
a. % EXPANSION vs CONCENTRATION (%) REACTIVE CONSTITUENT

A-	1.0	.9	.8	.7	.6	.5	.4	.3	.2	.1	0
B-	0	10(.1)	20(.2)	30(.3)	40(.4)	50(.5)	60(.6)	70(.7)	80(.8)	90(.9)	100
C-	0	.09	.16	.21	.24	.25	.24	.21	.16	.09	0
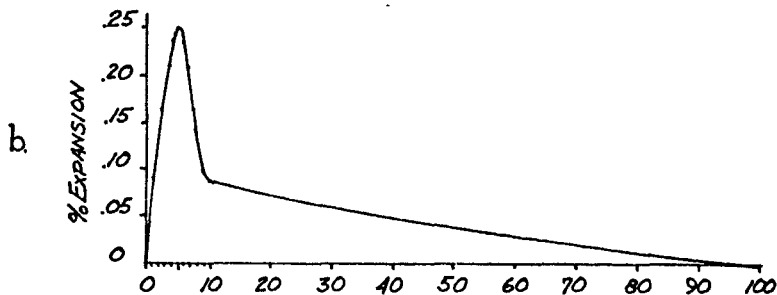
b. % EXPANSION vs CONCENTRATION (%) REACTIVE CONSTITUENT

A-	1.0	.9	.8	.7	.6	.5	.4	.3	.2	.1	.09	.08	.07 ...		.01
B-	0	1(.1)	2(.2)	3(.3)	4(.4)	5(.5)	6(.6)	7(.7)	8(.8)	9(.9)	10(.91)	11(.92)	12(.93)..	20..	30 etc
C	0	.09	.16	.21	.24	.25	.24	.21	.16	.09	.082	.074	.065.. etc		0%Exp
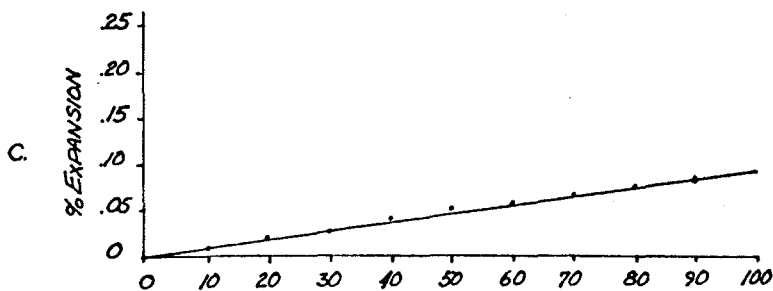
c. % EXPANSION vs CONCENTRATION(%) REACTIVE CONSTITUENT

A-	1.0	.99	.98	.97	.96	.95	.94	.93	.92	.91	.90
B-	0	10(.01)	20(.02)	30(.03)	40(.04)	50(.05)	60(.06)	70(.07)	80(.08)	90(.09)	100(.10)
C-	0	.01	.020	.029	.038	.048	.056	.07	.074	.082	.09

ATTACHMENT 1

Werner Furth
8/6/75

Suppose we have two reacting substances (call them X_1 and

X_2). Suppose that the initial value of X_1 and X_2 are such that

$X_1\big|_0 + X_2\big|_0 = 1$ (i. e., the total adds up to a fixed quantity).

Suppose further, that the rate of reaction of these two substances

is, at any moment, proportional to the amount left (k $X_1(t)$ $X_2(t)$).

Then, at small times, where there has not been a major depletion of

either X_1 or X_2, the rate of formation of the product (as well as

the amount of the product formed) is proportional to $X_{10} \cdot X_{20}$

which is $X_{20} (1 - X_{20})$ where X_{10} and X_{20} are the initial amount

of each reactive substance. Since $X_{20} (1 - X_{20})$ has a maximum at

$X_{20} = .5$, we have that, at a fixed time, the amount of product formed

first increases with an increase in X_{20}, then reaches a maximum,

and (for further increases in X_{20}) decreases to zero when $X_{20} = 100\%$.

For all times, the amount of product formed (y) is given by:

$$y = X_{20} - \frac{X_{20} (1 - 2X_{20})}{(1 - X_{20}) e^{kt (1 - 2X_{20})} - X_{20}}$$

which, for $kt\left|(1 - 2X_{20})\right| \ll 1$,

becomes $\quad y = X_{20} (1 - X_{20}) kt \quad$ (as noted above)

For large values of $kt \left|(1 - 2X_{20})\right|$

$$y = X_{20} \quad \text{if} \quad X_{20} < 1/2$$
$$y = 1 - X_{20} \quad \text{if} \quad X_{20} > 1/2$$