

EFFECT OF HYDRATION ON WATER SOLUBILITY
OF ALKALIES IN PORTLAND CEMENT

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Alkalies are becoming more important as components of cement because there is a tendency toward higher alkali contents. Some of the reasons for this increase in alkali contents are as follows:

1. Pollution controls now require that stack dust be collected. In most cases this dust is higher in alkali content than the kiln feed so when it is returned to the kiln it results in an increase in the alkali content of the clinker.
2. Because of the necessity for energy conservation many preheaters are being installed. In most cases these preheaters tend to retain the alkalies.
3. High sulfur coal is relatively low in cost and can be used to burn clinker without excessive SO_2 emission, however, it frequently results in an increase in the sulfate content of the clinker and this condition promotes the retention of alkalies in the clinker, particularly K_2O .

Until the last few years it was rather unusual for a cement to have an alkali content in excess of 1% but as a result of the foregoing this is not the situation any more. This increase in

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alkali content is significant not only because of the potential alkali-aggregate problems but also because of the important effect alkalies can have on strength and rate of strength gain, optimum SO_3 , performance with admixtures, etc.

Alkalies in portland cement clinker occur in many forms depending on:

- (1) Composition of kiln feed
- (2) Condition of burning - type of fuel
- (3) Rate of clinker cooling, etc.

Usually the alkalies combine with the available sulfate during the burning operation to form an alkali phase that contains both the K_2O and Na_2O with K_2O predominating. The amount of sulfate present usually is sufficient to combine with only part of the alkalies and the remaining portion combines with the aluminates and silicates with Na_2O principally in the aluminates and K_2O in the silicates.

When cement is mixed with water the alkali sulfates dissolve rapidly and the concentration of K_2O in solution is usually greater than Na_2O at very early ages. The other Na_2O phases tend to dissolve more rapidly than the K_2O phases since the aluminates hydrate more rapidly than the silicates. In view of the foregoing it would be expected that the portion of alkalies that are water soluble after any given period of hydration can vary considerably depending on the clinker. This variation in the portion of the alkalies that are water soluble is illustrated by Figs. 1, 2, and 3 which show both the total and water-soluble alkali contents for a number of

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Type I, II, and III cements, respectively. The total and water soluble alkalies were determined by ASTM Method C 114. It is interesting to note that on the basis of this series of tests the amount of alkali in a cement that is water soluble can vary from less than 10% to over 60% of the total alkali present.

FIGURE 1

**% TOTAL ALKALIES AS Na₂O EQUIVALENT VS. WATER SOLUBLE ALKALIES
AS Na₂O EQUIVALENT - TYPE I CEMENT**

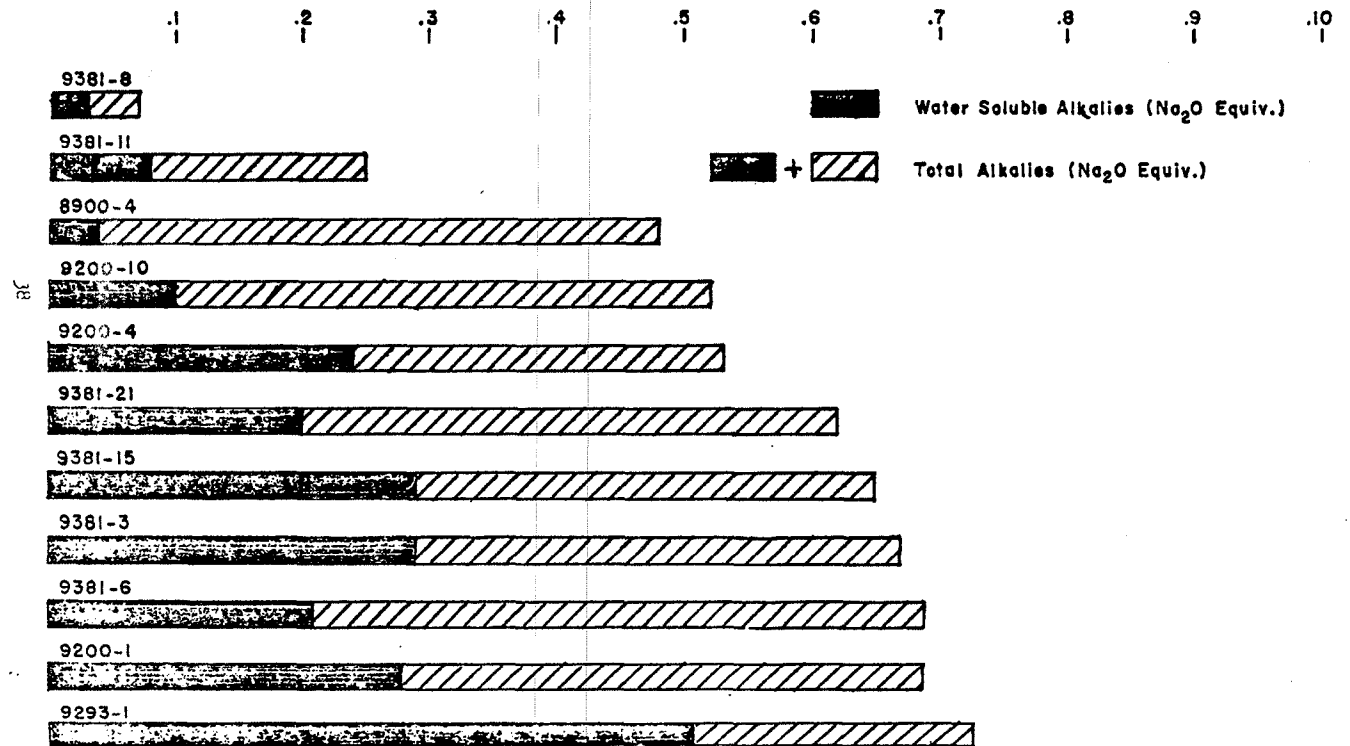


FIGURE 2

% TOTAL ALKALIES VS. % WATER SOLUBLE ALKALIES - TYPE II CEMENTS

FIGURE 2

% TOTAL ALKALIES VS. % WATER SOLUBLE ALKALIES - TYPE II CEMENTS

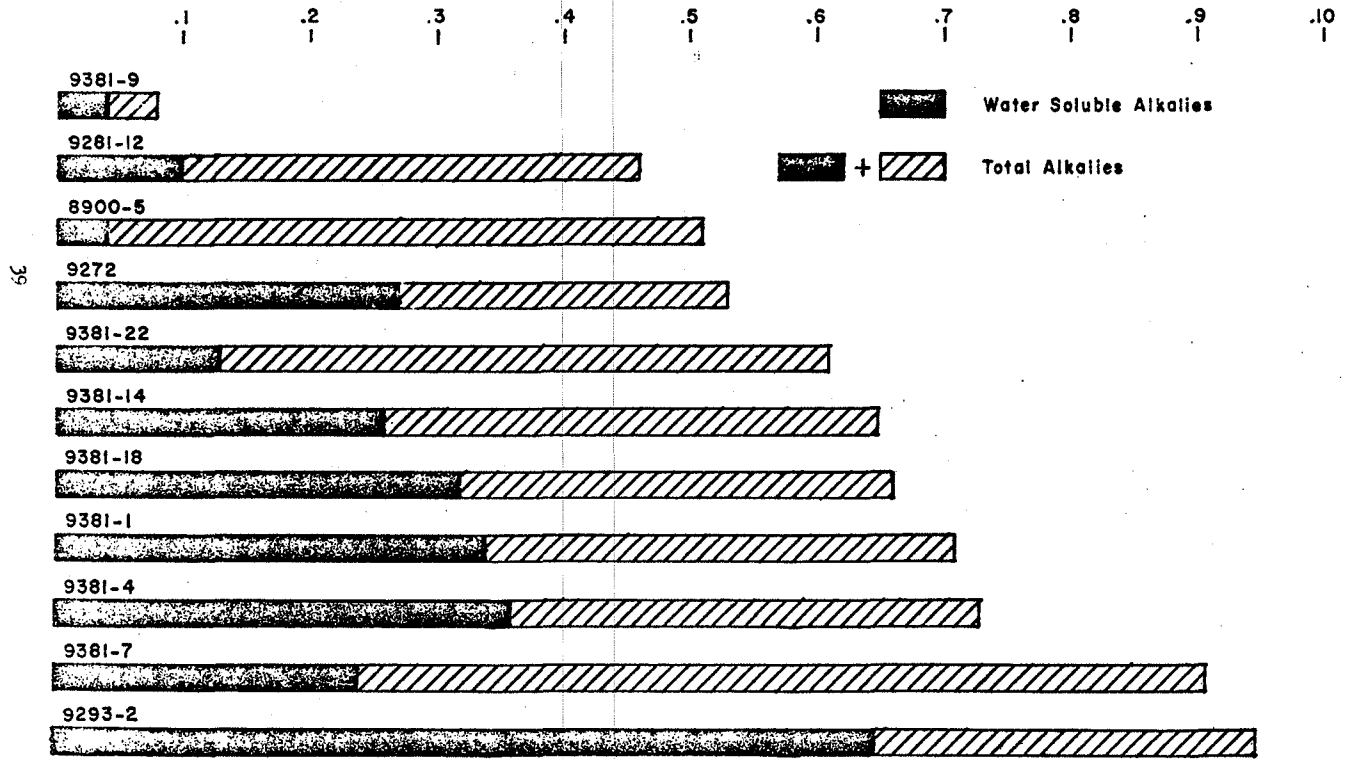
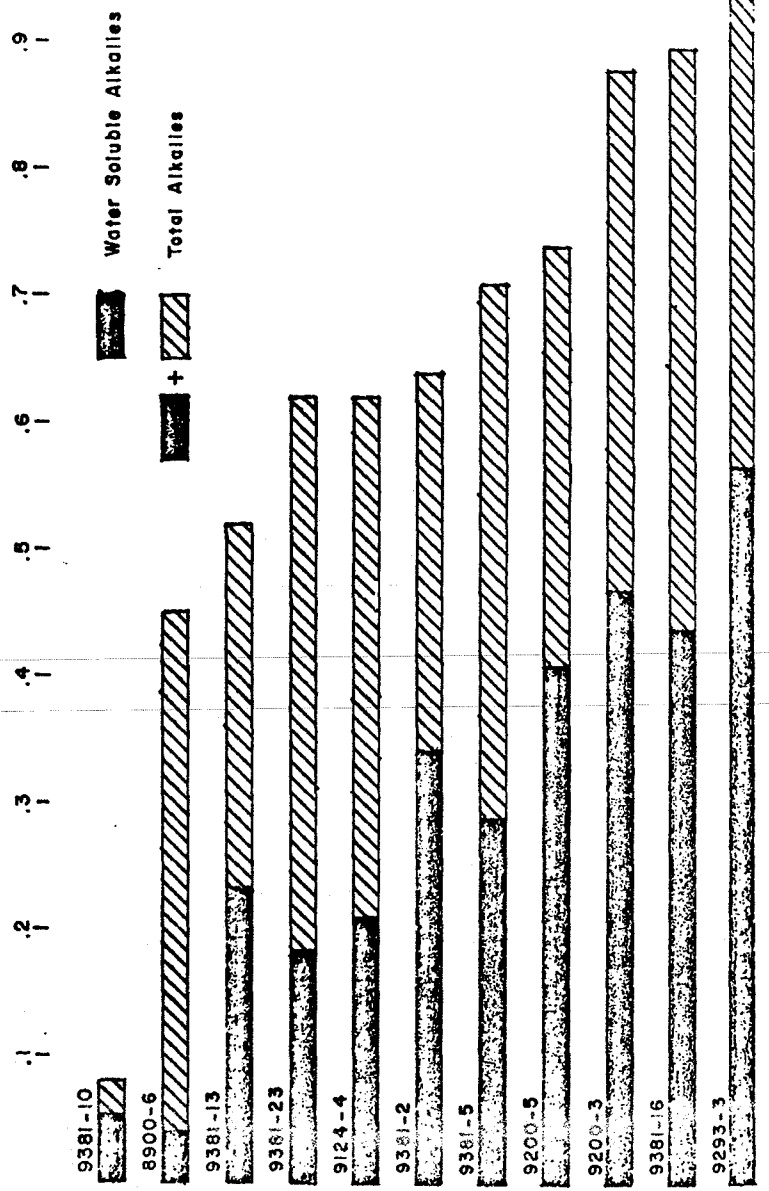


FIGURE 3

% TOTAL ALKALIES VS. WATER SOLUBLE ALKALIES - TYPE III CEMENTS



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% K₂
1st
2nd
3rd

% Na
1st
2nd
3rd

Total

% K₂
% Na

Information regarding the rate of solution of the alkalies was obtained by an elaboration of ASTM Method C 114 whereby the soluble alkalies were determined in each of three successive leachings at 30 minute intervals. These data are given in Table I and show that after two successive leachings very little, if any, more alkali is dissolved by additional extractions. The total alkali (acid soluble) of the cements are listed in the table for convenient reference:

Table I

Water Soluble Alkalies, Type I Portland Cement
Successive Leachings - ASTM Method C 114

	<u>8658-1</u>	<u>8660-3</u>	<u>8662-1</u>	<u>8864-3</u>
<u>% K₂O</u>				
1st	.44	.36	.37	.10
2nd	.14	.06	.06	.02
3rd	.02	.01	.01	.00
<u>% Na₂O</u>				
1st	.03	.09	.03	.02
2nd	.01	.02	.00	.00
3rd	.00	.00	.00	.00
<u>Total Alkali (Acid Soluble)</u>				
% K ₂ O	1.10	.71	.77	.56
% Na ₂ O	.14	.36	.13	.26

A series of tests were made on neat cement bars prepared as in ASTM Method C 151 to determine what effect hydration of cement at 23° C would have on the solubility of the alkalies. The bars were stored in a moist closet with relative humidity in excess of 90%. After storage, the hydrated bars were crushed, dried at 100° C and ground to the same approximate fineness as the cement was originally. The water of hydration was determined at ages of 1 month and 1 year and is shown in Table II.

Table II

Percent Ignition Loss of Hydrated
Type I Cements (Dried at 110° C)

	<u>1 Month</u>	<u>1 Year</u>
8658-1	13.5	15.7
8664-3	14.6	16.1
9293-1	14.0	15.5

Table III shows the amount of total and water soluble alkalies of unhydrated cement and also the amount of the alkalies that are soluble after hydration for a year with appropriate corrections being made for water of hydration as noted in Table II. The data in Table III is quite interesting because even after hydration for a year a large portion of the alkalies remain insoluble and in one case there was less alkali soluble after one year hydration than there was originally.

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Table III

Effect of Hydration For 1 Year On the Solubility of Alkalies
in Type I Cement

<u>Unhydrated</u>	<u>8658-1</u>	<u>8664-3</u>	<u>9293-1</u>
Total K ₂ O, %	1.1	.56	.74
Total Na ₂ O, %	<u>.13</u>	<u>.26</u>	<u>.25</u>
Total Alkali, %	1.23	.82	.99
Water Soluble K ₂ O, %	.68	.10	.57
Water Soluble Na ₂ O, %	<u>.03</u>	<u>.02</u>	<u>.11</u>
Water Soluble Alkali, %	.71	.12	.68
% of Alkali, Water Soluble	58	15	68
<u>Hydrated 1 Year</u>			
Water Soluble K ₂ O, %	.71	.22	.45
Water Soluble Na ₂ O, %	<u>.08</u>	<u>.16</u>	<u>.15</u>
Water Soluble Alkali, %	.79	.38	.60
% of Alkali, Water Soluble	64	46	60

The test results shown in Table III were somewhat unexpected and in need of confirmatory data. This was obtained in another series of similar tests on three other samples of cement and the results are shown in Table IV.

Table IV

Effect of Hydration For 1 Year On the Solubility of Alkalies
in Type I Cement

<u>Unhydrated</u>	<u>8664-8</u>	<u>8662-1</u>	<u>8658-5</u>
Total K ₂ O, %	.29	.77	.59
Total Na ₂ O, %	<u>.65</u>	<u>.13</u>	<u>.23</u>
Total Alkali, %	.94	.90	.82
Water Soluble K ₂ O, %	.09	.45	.24
Water Soluble Na ₂ O, %	<u>.08</u>	<u>.03</u>	<u>.03</u>
Total Soluble Alkali, %	.17	.48	.27
% of Alkali, Water Soluble	18	53	33
<u>Hydrated 1 Year</u>			
Water Soluble K ₂ O, %	.05	.17	.10
Water Soluble Na ₂ O, %	<u>.20</u>	<u>.05</u>	<u>.07</u>
Total Soluble Alkali, %	.25	.22	.17
% of Alkali, Water Soluble	27	24	21

The data in Table IV show that in this series of tests two of the cements had less of the alkali soluble after 1 year hydration than was soluble in the unhydrated cement. This was due to the decrease in the solubility of the K₂O.

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In conclusion it appears appropriate to comment that the foregoing data suggests that perhaps the alkali limit with regard to the potential alkali-aggregate reaction should be based on the soluble alkali content of the cement rather than the total alkali content. Also when studies are made to correlate other properties of cement such as optimum SO_3 , rate of strength gain, etc. with the alkali content, attention should be given to the soluble alkali content.

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