The Effect of Sulfur to Alkali Ratio on Clinker Properties

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ABSTRACT: The usage of alternative fuel and raw material (AFR) as bio-mass in the cement industry has been increased due to the higher cost of conventional energy. These AFR are composed of many minor elements especially alkali and sulfur. The aim of this study is to better understand the influence of alkali and sulfur in AFR on clinker properties. The laboratory testing was conducted by using potassium carbonate (K_2CO_3) as a source of alkali and ammonium sulfate as a source of sulfur and using clinker samples from Lampang Cement Plant. All raw mix samples were burnt in electrical furnace at 1450 ^oC. The laboratory and plant samples were tested by XRD qualitatively and quantitatively with calibration line method, Only Aluminate phase was obtained by salicylic acid in methanol extraction method (SAM) and minor element in aluminate phase was measured by SEM-EDS method. It was found that alkali enriched raw mix led to formation of orthorhombic C_3A in spite of cubic polymorph in laboratory clinker which made the reactivity of cement higher. The high SO_3 in alkali rich raw mix led to minor compounds formation in laboratory clinker that consisted mainly of arcanite and calcium langbeinite. These minor compounds affected water requirement of cement and workability of concrete. Moreover it was found from testing results of plant clinker that the molar ratio of sulfur to alkali about nearly 1.0 would promote the highest alite content. But formation of arcanite and calcium langbeinite was increased with the increasing sulfur to alkali ratio.

1. Introduction

Changes in the cement manufacturing process, such as the usage of higher sulfur alternative fuels and raw materials have tended to increase the amount of sulfate in clinker and sulfur to alkali ratio. Consequently, the nature and quantity of the clinker phases have been modified and promoted alkali sulfate formation. Clinker sulfates tend to be available as double sulfate salts; calcium langbeinite and potassium sulfate.

AFR consists of alkali element mainly potassium and sodium that can affect clinkering process and cement properties. Two alkalis prefer to incorporate in belite and aluminate phase than others. When liquid phase forms in clinkering process, alkali element can reduce temperature of liquid phase formation but raise viscosity of liquid phase in absence of sulfur. Furthermore, aluminate phase has been modified by alkali leading to formation of orthorhombic aluminate. It can have undesirable effect on the rheology of fresh concrete

Generally, sulfur is introduced in clinker from fossil fuel and some raw materials as well as alternative raw materials. Sulfur can react with alkali from raw materials to form alkali sulfate that can be entrapped in the clinker grain. Clinker chemical and crystallography can be modified in the presence of sulfur in the clinkering process. Sulfur is preferentially incorporated in the belite phase. Belite and free CaO tend to be stabilized at clinkering temperature resulting in decreasing alite content and increasing free CaO.

Clinker produced using an alternative fuels, and raw materials has been analyzed to identify the clinker sulfate phases. Quantitative X-ray diffraction methods were used in conjunction with extraction procedures to concentrate or extract the sulfate phases. The minerals were aphthitalite ($3K_2SO_4.Na_2SO_4$), arcanite (K_2SO_4), calcium langbeinite ($K_2SO_4.2CaSO_4$) and thenardite (Na_2SO_4). Overall sulfur content in clinker increased in proportion with the amount of sulfur in the fuel. The distribution of sulfur in clinker was identified its presence as alkali sulfates, alkali calcium sulfates and sulfate incorporated in the silicate phases. The selective dissolution procedure by salicylic acid in methanol extraction method (SAM) is applicable to the evaluation of sulfate distribution of both clinker and finished Portland cement.

2. Experiment

2.1 Laboratory clinker sample preparation

Laboratory clinkers were prepared by using potassium carbonate (K_2CO_3) as a source of alkali and ammonium sulfate as a source of sulfur mixed with rawmeal from Lampang Cement Plant. The complete chemical analysis results of the rawmeal used in this study were shown in table 1.

Table 1 The chemical composition of rawmeal from Lampang Cement Plant

Oxide %	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3	Na_2O	LOI
Rawmeal	12.12	2.81	1.69	44.85	1.25	0.4	0.07	0.08	35.57

All samples can be divided into two series. First series was aimed to study the effect of alkali on clinker properties including chemical, crystallography and reactivity. Samples were mixture of rawmeal and potassium carbonate in proportion which was shown in table 2.

Table 2 The proportion of rawmeal and potassium carbonate mixture

Sample code		K0	K1.5	K2.5	K3.0
Rawmeal	%	100.0	98.5	97.5	97.0
Potassium carbonate	%	0.0	1.5	2.5	3.0

Second series was aimed to investigate the combination effect of alkali and sulfur on clinker properties including chemical, crystallography and reactivity and to study the optimum of sulfur to alkali ratio that was considered to be the important factor to control the clinker characteristic. All samples were prepared by mixing rawmeal, potassium carbonate, and ammonium sulfate in proportion was shown in table 3

Table 3 The proportion of rawmeal, potassium carbonate and ammonium sulfate mixture

Sample code	Rawmeal %	Potassium carbonate%	Ammonium sulfate%
K1.5S0	98.5	1.5	0
K1.5S1	98.5	1.5	1.0
K1.5S1.5	98.5	1.5	1.5
K1.5S2.4	98.5	1.5	2.4
K2.5S0	97.5	2.5	0
K2.5S1	97.5	2.5	1.0
K2.5S1.5	97.5	2.5	1.5
K2.5S2.4	97.5	2.5	2.4
K3.0S0	97.0	3.0	0
K3.0S1	97.0	3.0	1.0
K3.0S1.5	97.0	3.0	1.5
K3.0S2.4	97.0	3.0	2.4

All samples of two series were ground and mixed in the high speed mill until the fineness of mixture was to be 10% residue on sieve 90 micrometer. The ground sample was mixed with water approximately 5-10% to make granule of 5 millimeter diameter. Then the granule was dried in room temperature for a half-day. After that all samples were contained in platinum crucible covered with platinum lid and burnt in the electrical furnace at burning temperature 1,450 ^{o}C for 1 hour. After thorough burning all laboratory clinker samples were brought out of the electrical furnace at the temperature 1,300 ^{o}C and cooled to room temperature. Then, all clinker samples were ground in the high speed mill to obtain the air permeability fineness 3,300 cm^2/g.

2.2 Lampang cement plant clinker sample preparation

Lampang cement plant clinker samples were collected from cement plant by varying the alkali and sulfur content in the clinker. The lime saturation factor, silica modulus, alumina modulus and free CaO of clinker sample were analyzed in order to eliminate the undesirable variable factor. Then, all clinker samples were ground in the high speed mill to obtain the air permeability fineness 3,300 cm^2/g.

2.3 Chemical composition analysis by SEM-EDS

All laboratory clinker samples were measured the amount of K-element and S-element in clinker phase by SEM-EDS method

2.4 Clinker phases crystallographic analysis

All ground laboratory clinker samples were ground in the high speed mill in order to reduce particle size to less than 45 micrometer. The obtained sample was divided into two groups. First group sample was then pressed in sample holder and analyzed by X-ray diffractometer to determine the quality and quantity of clinker phases. The other was extracted silicate phases from aluminate phases by salicylic acid in methanol extraction method (SAM). The extracted sample was then analyzed by XRD to identify the polymorphism of C_3A phase. All ground plant clinker samples were ground in the high speed mill in order to reduce particle size to less than 45 micrometer and was then pressed in sample holder and analyzed by X-ray diffractometer to determine the quantity of clinker phases.

2.5 Heat of hydration of extracted clinker

For the laboratory clinker sample, the extracted samples were mixed with 25 % by weight of gypsum in order to keep the SO_3 to aluminate ratio of 1:4. After thorough mixing, all samples were mixed with water and immediately contained in foam container. The samples were measured temperature at the center of sample by data logger as shown in figure 1.

Figure 1 The rate of heat evolution method

2.6 Mini slump test for cement sample

For laboratory cement sample, the cement samples was prepared by combining and mixing between type I Portland cement and potassium sulfate (K_2SO_4) according to proportion that was shown in table 4. The cement sample was mixed with water at w/c 0.4 for 1 minute and was then placed in mini-slump mold. The workability of cement sample was measured in term of spreading out distance from center.

Table 4 The mixture of type I Portland cement and potassium sulfate

Sample code		KS0	KS1.8	KS2.1	KS3.0
OPC	%	100.0	98.2	97.9	97.0
Potassium sulfate	%	0.0	1.8	2.1	3.0

3. Results and discussions

Chemical composition results of laboratory clinker samples were shown in figure 1, alkali as potassium dioxide could incorporate in to the laboratory clinker samples without volatile at the clinkering temperature. The sulfur could also incorporate into the laboratory clinker sample that was shown in figure 2 but sulfur could be volatized at clinkering temperature therefore the sulfur content in clinker was lower than the sulfur that was added into the rawmeal.

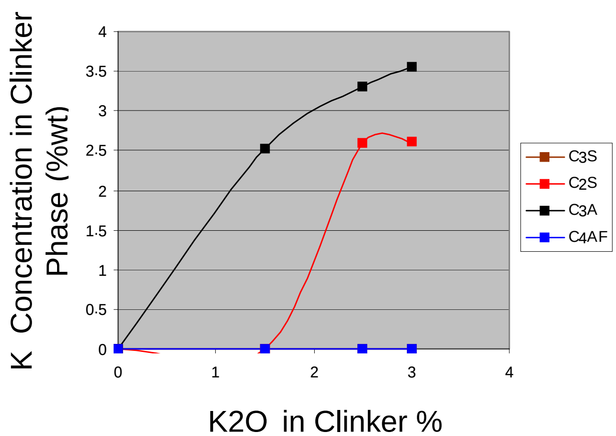


Figure 1 the K-element distribution in clinker phase

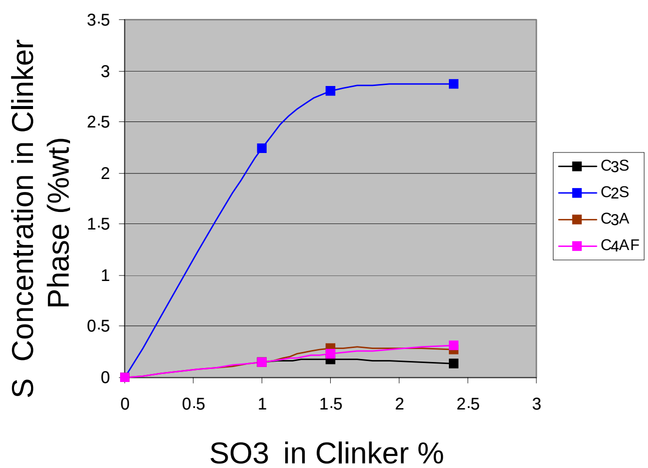


Figure 2 the S-element distribution in clinker phase

For the laboratory clinker sample which were added only potassium carbonate, crystallographic results were shown in the figure 3, it was found from this experiment that the clinker phase especially C_3A phase could be modified by the potassium oxide. The most commercial clinker with low alkali content, crystallography of C_3A phase was found to be only cubic form but an addition of alkali in clinker was able to change the cubic form to orthorhombic form because alkali could incorporate in to the C_3A crystal and modified the crystal structure or unit cell parameter of C_3A. The amount of orthorhombic form of C_3A was increased with alkali content.

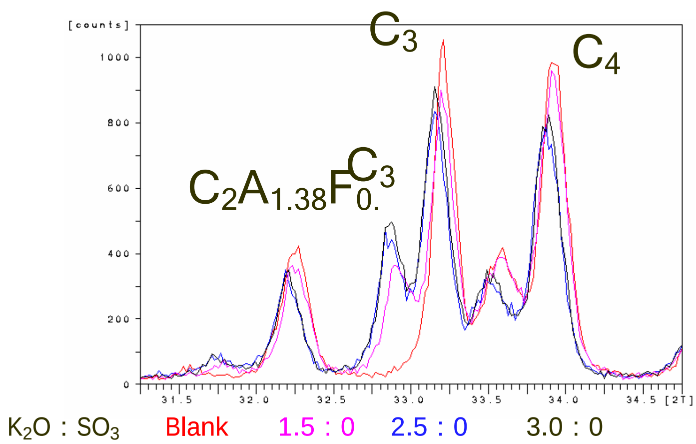
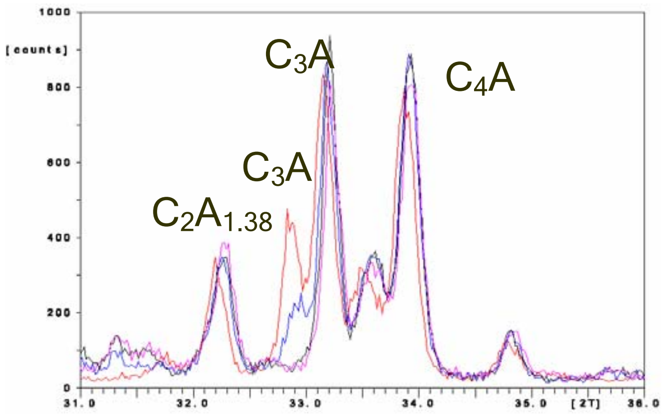


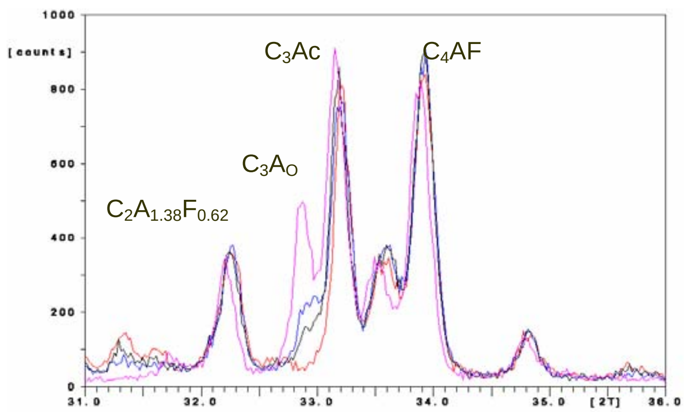
Figure 3 The crystallography of C_3A phase with potassium carbonate

For the laboratory clinker sample which were added potassium carbonate and ammonium sulfate, crystallographic results were shown in the figure 4 to 6, the results showed that the clinker phase formation especially C_3A phase was depended on the amount of alkali and sulfur in clinker. By adding the ammonium sulfate in the added alkali clinker samples, the amount of orthorhombic form C_3A was decreased and the amount of cubic form C_3A was increased. The alkali sulfate especially arcanite (K_2SO4) and syngenite ($K_2Ca(SO_4)_2.H_2O$) in laboratory clinker was increased with ammonium sulfate as shown in figure 7.



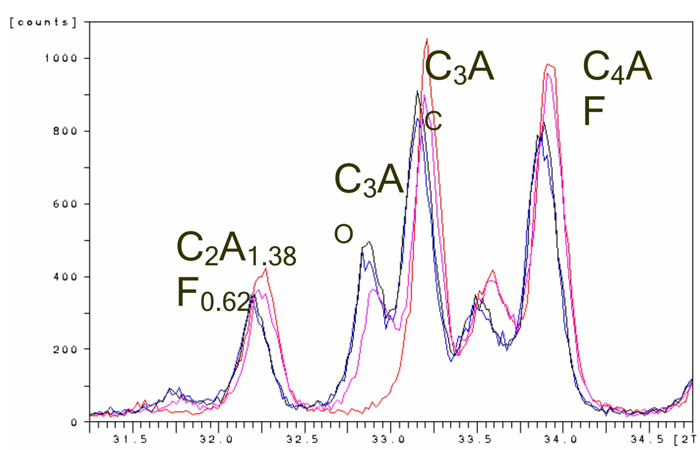
K_2O : SO_3 1.5 : 0 1.5 : 1.0 1.5 : 1.5 1.5 : 2.4

Figure 4 The crystallographic of C_3A phase with potassium carbonate 1.5 % and ammonium sulfate



K_2O : SO_3 2.5 : 0 2.5 : 1.0 2.5 : 1.5 2.5 : 2.4

Figure 5 The crystallographic of C_3A phase with potassium carbonate 2.5 % and ammonium sulfate



K_2O : SO_3 3.0 : 0 3.0 : 1.0 3.0 : 1.5 3.0 : 2.4

Figure 6 The crystallographic of C_3A phase with potassium carbonate 3.0 % and ammonium sulfate

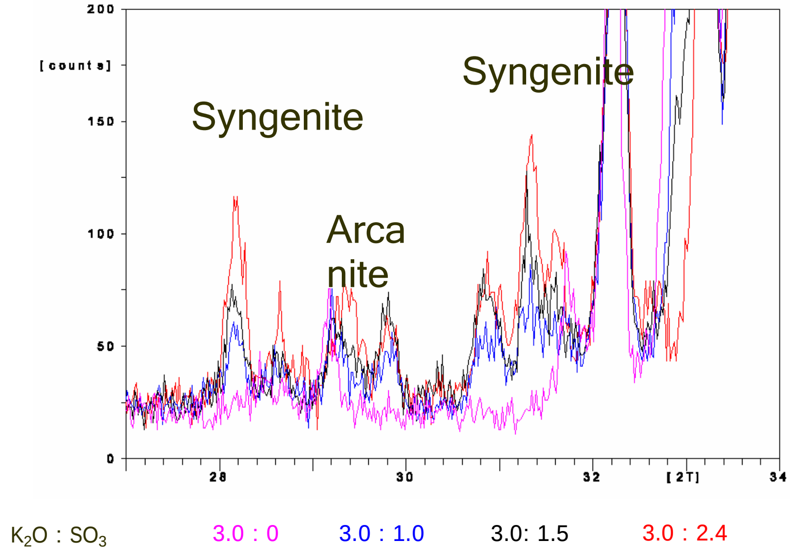


Figure 7 The alkali sulfate as function of ammonium sulfate

For the laboratory clinker sample which were added only potassium carbonate, rate of heat of hydration results were shown in the figure 8. It was found that for added potassium carbonate clinker samples the rate of heat evolution was slower than that of clinker sample without potassium carbonate. This result was due to reactivity of orthorhombic form of C_3A was lower than that of cubic form of C_3A. It was confirmed in the clinker phase crystallographic analysis result that an addition of alkali in clinker was able to change the cubic form of C_3A to orthorhombic form of C_3A.

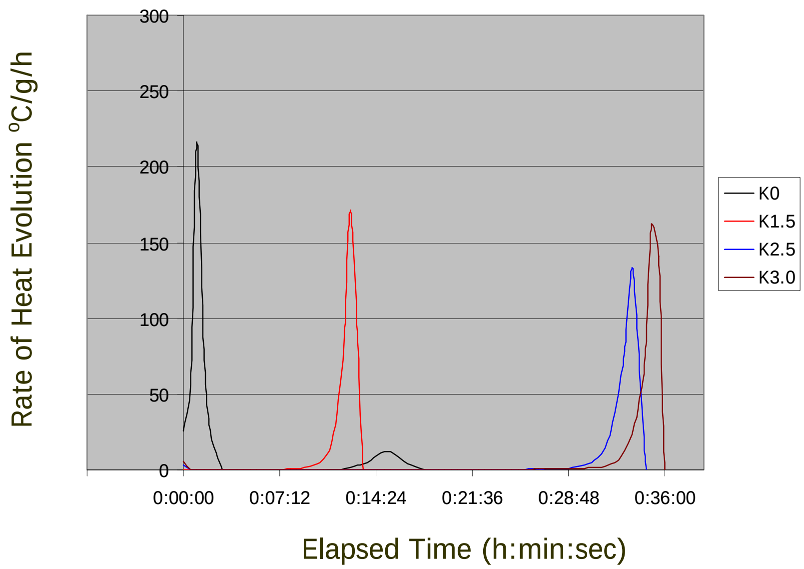


Figure 8 The rate of heat evolution as function alkali content

For the laboratory clinker samples which were added potassium carbonate and ammonium sulfate, were shown in the figure 9. The results shown that for added potassium carbonate and ammonium sulfate clinker samples as well as clinker sample without potassium carbonate and ammonium sulfate, the rate of heat evolution was faster than that of added only potassium carbonate clinker sample. This result because the sulfate was able to combine and react with alkali to form alkali sulfate therefore remained alkali content was low and cubic form of C_3A wasn't modified. It was confirmed from the clinker phase crystallographic analysis result that the amount of orthorhombic form of C_3A was decreased and the amount of cubic form of C_3A was increased by adding the ammonium sulfate. Furthermore, it was found that the alkali sulfate especially arcanite (K_2SO_4) and syngenite ($K_2Ca(SO_4)_2.H_2O$) in laboratory clinker can be occurred and increased with ammonium sulfate.

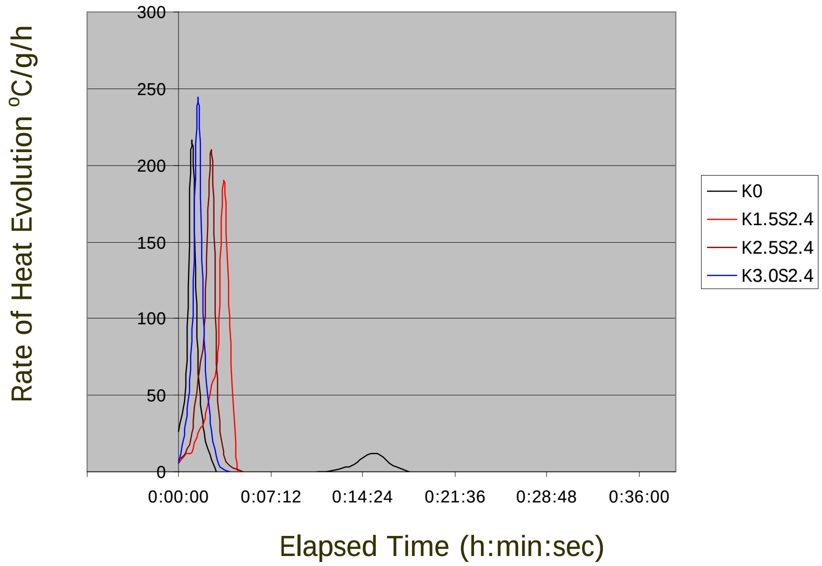


Figure 9 The rate of heat evolution as function sulfur and alkali content

For laboratory cement sample mixed with potassium sulfate, mini-slump testing result was shown in figure 10. The result showed that mini-slump was decreased with increasing amount of K_2SO_4. Therefore, it implied that the workability of cement that composed of alkali sulfate was not good thus higher water requirement of concrete is to be important factor for controlling the compressive strength of concrete.

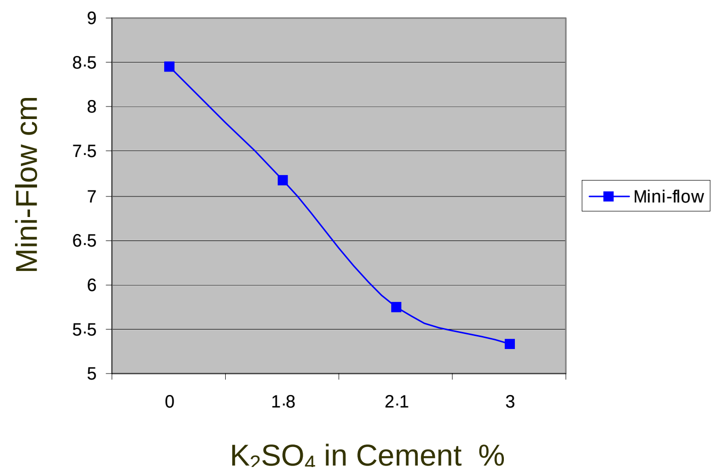


Figure 10 The mini-slump result of cement containing K2SO4

Finally, for the plant clinker samples, from the quantitative XRD with calibration line method and sulfur to alkali molar ratio results as shown in figure 11 that amount of C_3S was decreased with sulfur to alkali molar ratio. Because alkali could inhibit C_3S formation in clinker resulting decreasing in C_3S content. It was found that alkali could stabilize C_2S and CaO at clinkering temperature. It could be corrected by balancing sulfur to alkali molar ratio. Additional, the amount of C_3S was maximum about 55% when sulfur to alkali molar ratio was approximate 1.0. In contrast, the alkali sulfate can be increased with sulfur to alkali molar ratio.

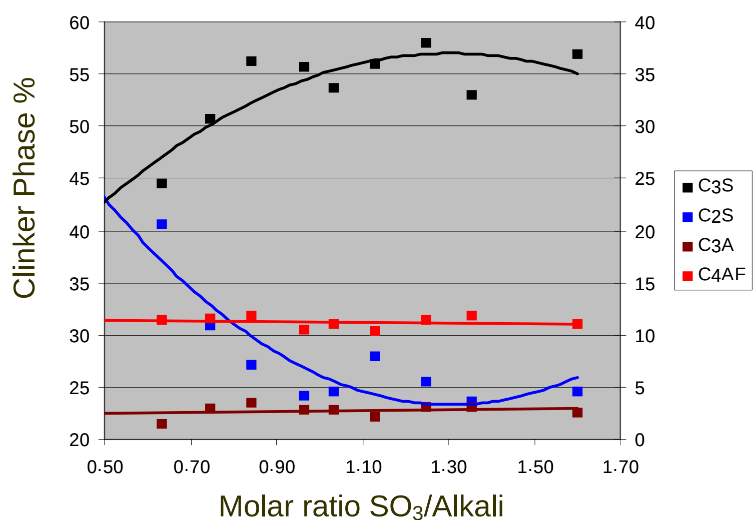


Figure 11 The sulfur to alkali molar ratio

4. Conclusions

It was found that the alkali enriched raw mix led to the formation of C_3A orthorhombic in spite of cubic polymorph in laboratory clinker which made the reactivity of cement higher. The high SO_3 in alkali rich raw mix led to minor compounds formation in laboratory clinker that consisted mainly of arcanite and calcium langbeinite. These minor compounds affected the water requirement of cement and the workability of concrete. Moreover it was found from the testing results of plant clinker that the molar ratio of sulfur to alkali is nearly 1.0 could promote the highest alite content. But formation of arcanite, calcium langbeinite was increased with increasing sulfur and alkali ratio. This research results could be helped production performance of Lampang cement plant.

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