

Minerological aspects of lead sintering

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ABSTRACT

A brief overview on lead sinter microstructure is presented. Characteristic micro-structural features of a good and bad sinter are highlighted and these are used in a case study involving use of a low grade and complex concentrate of lead (~40% Pb) in the sintering operation. The plant sinter produced exhibited low strength and its microstructural examination revealed non-uniform distribution of porosity along with unsintered galena and low melting lead silicate phase. Part replacement of limestone by lime helped in producing sinter with good physical properties and desirable microstructure. The sinter with modified feed chemistry had more uniform distribution of porosity and presence of primarily a Pb-Fe silicate phase characterised by a (Pb+Fe):Si mole ratio of 3:1, Ca-Pb-Zn-Fe-Al-silicate phase identified as hardysonite and a spinel phase of the type (Fe,Zn)O.(Fe,Al)₂O₃. Lead metal/oxide/sulphide occurred in the sinter only rarely. The likely implications of lime addition to the sinter charge mix are discussed

Key Words: Lead, Complex and low grade concentrate, Sintering, Process Mineralogy

INTRODUCTION

In the recent past, a large number of primary lead production processes have been developed on commercial scale (example: QSL process, imperial smelting) together with significant advances in the secondary lead processing. World-over, the conventional blast furnace reduction route continues to be in use in several plants. Sintering of lead concentrate, that has twin objectives of sulphur removal through oxidation and agglomeration, is a key unit process prior to the reduction in the blast furnace. In the sintering process, sulphide concentrate(s) are mixed with return sinter fines along with limestone, iron ore, quartz (fluxes) and blast furnace slag and desulphurised in a sinter machine to get a sinter suitable for the blast furnace. The performance of a sintering operation is judged by the produc-

tivity and quality of sinter produced. The parameters which define the quality of sinter are its sulphur content, room temperature strength, porosity, degradation behaviour and softening characteristics.

There have been several attempts to study the mineralogy of sinters and correlate it with sinter characteristics¹¹⁻⁷¹. The quality of sinters is directly linked with the mineralogy, i.e., minerals and microstructures present. Good sinters form competent masses, approximately 10-15 cm across, that have approximately 15% porosity and good mechanical strength to withstand transport and weight of the overlying load in the smelter. Holiday *et al*²¹ addressed the problem of premature softening of lead sinter fed to the ISF furnace of Sulphide Corporation Pty Limited at Cockle Creek, New South Wales, Australia. The problem of premature softening was attributed to the increasing silica content in the sinter, which led to the formation of a low melting glass phase containing calcium and lead oxide. With an understanding of correlation between microstructure and softening behaviour of sinter, changes in the feed composition, in terms of basicity and Fe_2O_3 content, were suggested to get the desired microstructure, consisting of high melting point calcium ferrite eutectic as binder, and overcome the problem of premature melting. Recently, Hagni and co-workers^{13,41} have attempted mineralogical characterisation of good and bad sinters using reflected light microscopy with X-ray microanalysis (SEM-EDS) and electron microprobe. Based on these studies^{13,41}, the mineralogical characteristics of good and bad sinters are summarised in Table 1. In the studies on sinter samples, produced using lead concentrate from Viburnum in south-east Missouri, it was found that good sinters consist predominantly of hardysonite, franklinite, lead silicate matrix and large crystals of calcium-magnesium-iron silicate, together with minor amounts of lead oxides, lead-zinc silicate, metallic lead, specular hematite, magnetite, Pb-Fe bearing zincite, and Zn-Pb-Mg bearing wustite in a tightly inter-grown mesh of crystals and with an evenly distributed porosity of approximately 15-20%. Bad sinters contain larger amounts of lead silicate matrix, galena, metallic Pb, and lead oxides, but smaller amounts of hardysonite, franklinite, and calcium-magnesium-iron silicate, lack intimate growth of phases, and have lower (0-5%) and unevenly distributed porosity. Huyssteen *et al*¹⁵¹ have developed a method of establishing the relationship between the mineralogy of a sinter and its subsequent processing behaviour in the lead blast furnace. These studies have demonstrated that not only the sinter microstructure is important but also equally important is the distribution of elements into various phases in the sinter. Specifically, the substitution of Mg for Zn in hardysonite significantly influences sinter production. Magnesium substitution releases Zn into the surrounding matrix. This Zn reacts with the lead-silicate to form larsenite thereby reducing the amount of lead-silicate available for anhydrite digestion. Excessive amounts of residual anhydrite thus result if the sinter formulation is based solely on the CaO/SiO_2 .

Recently, Lee *et al*^[6] have established that solidification of complex PbO-ZnO-Fe₂O₃-CaO-SiO₂-Al₂O₃-MgO could be represented by pseudo ternary phase diagrams of the lead oxide-melilite-franklinite system comprising of three binary eutectics and one ternary eutectic. The diagram has been found useful in representing the formation of phases in lead blast furnace sinters. Besides temperature history of the sinter bed (typical sintering temperature 1000-1050°C), the formation phases in the sinter is primarily controlled by the feed chemistry^[7,8].

Table 1 : Mineralogical Characteristics of good and bad sinters

Good Sinter	Good Sinter
Porosity (15-20%)	Low porosity (0-5%)
Uniform distribution of porosity	Uneven distribution of porosity
Minerals predominantly present	Minerals predominantly present
- Hardysonite (Ca ₂ ZnSi ₂ O ₇)	- Lead silicate (excess amount)
- Wollastonite (CaSiO ₃) (4-20% Pb)	- Galena (PbS)
- Franklinite [(Zn,Fe) Fe ₂ O ₄ (2-14% Pb)	- Metallic lead
- Lead silicate (matrix) (~70% Pb)	- Lead oxides
- Ca-Mg-Fe silicate	Lack of intimate growth of minerals
Intimate growth of minerals	

Background Information

The problem of low quality sinter and productivity was encountered in a lead-plant that used partially (30-50% of the total concentrate) a low grade lead concentrate containing as low as 35-40% lead and abnormally fine granulometry. The complexity of the feed was further compounded by the presence of large amount of acid insoluble silicate gangue (25-30%) and 4-9% carbon (possibly in the form of graphite) in the concentrate. Typical sulphur level in the sinter was near 2%. The sinter from the plant showed non-uniform microstructure and uneven distribution of porosity (Fig.1). SEM-EDS studies revealed presence of unsintered or partially sintered galena and lead silicate phase (Pb/Si = 1) surrounding unsintered or partially sintered galena. Literature revealed that the PbO.SiO₂ phase is low melting (761°C)^[3].

The complex nature of the concentrate manifested itself in several ways. In the sintering experiments on the pellets (without any addition) of different kinds of concentrate in a muffle furnace at 975°C, the pellets of the low-grade concentrate melted completely in sharp contrast with the pellets made from a high-grade concentrate. This corroborated formation of low melting phases at the sintering

temperature. Studies on the sintering of three types of fluxed pellets (basicity similar to plant-sinter) made from pure galena, galena and carbon and the concentrate revealed the following: (a) phases formed in a good sinter could be reproduced in the sinter pellets prepared using only galena, primarily Pb-Ca-Silicate phases either rich in lead or calcium; (b) presence of graphite during sintering of galena did not alter the nature of phases formed and its only effect was on small alteration in porosity distribution from even to somewhat uneven; (c) highly complex phases and very uneven distribution of porosity was observed when pellets containing the concentrate were sintered indicating more detrimental role of insoluble gangue. The problem of sintering was investigated further by carrying out batch sintering tests in the laboratory using the low grade complex concentrate with a high grade concentrate (65% Pb) and similar charge mix as used in the plant. Detrimental effect of the complex concentrate showed more and more with its increasing amount in the feed. In a typical sintering test carried out using 70:30 proportions of the low and high grade concentrates, sulphur level in the sinter was about 2% and the sinter showed all the microstructural features of a bad sinter, for example completely fused regions and unsintered galena crystals. SEM-EDS characterization of the polished sections of some of the sintered lumps indicated presence of a irregular shaped white colour calcium silicate phase (Ca:Si=1) distributed in dark heterogeneous matrix that showed the presence of Fe, Zn, Ca, Si and S along with small amount of lead (Fig. 2). The matrix appeared to be quite complex at higher magnification. Small crystals of lead sulphide were found randomly distributed in the matrix phase. Very encouraging results were observed with regards to sinter microstructure when a part of limestone was replaced by lime. Effect of lime substitution was investigated in detail and these results are reported in this paper.

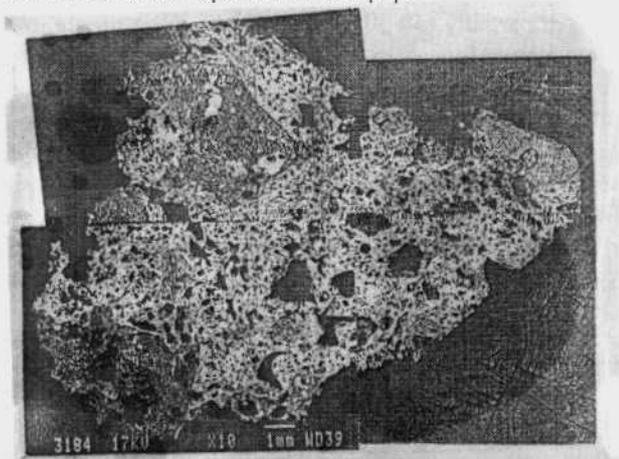


Fig. 1 : Typical polished section of the sinter sample

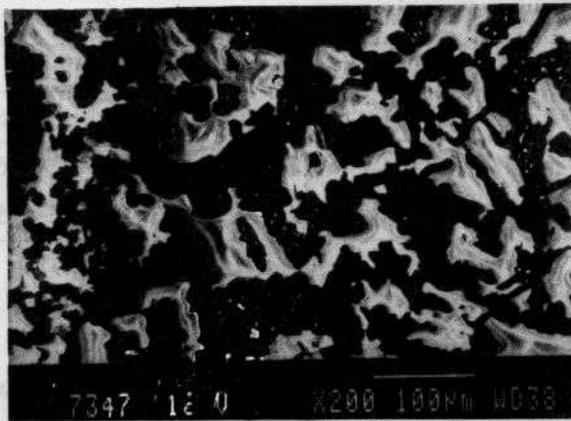


Fig. 2 : SEM micrograph showing presence of an irregular shaped white colour calcium silicate phase (Ca : Si = 1) distributed in the matrix comprising of Fe, Zn, Ca, Si and S along with small amount of lead

EXPERIMENTAL DETAILS

Pot-grate sintering studies were carried in a 200 x 200 x 400 mm³ down draft sinter pot using a 30 kg charge mix. The charge mix fed to the sinter pot consisted of the lead sulphide concentrate, return sinter, limestone, lime (as a part replacement for limestone), iron oxide and blast furnace slag. The chemical composition of major constituents, namely the lead concentrate and return fines used is given in Table 2. The sintering conditions and charge mix composition used in some of the representative tests are given in Table 3. The prime focus in the investigation was on the sinter basicity and proportion of lime and limestone. The sinter samples were characterised in terms of chemical composition, physical strength (Shatter and Tumbling Tests) and mineralogical features (phases present and microstructure). Representative coarse (+10 mm) sinter samples were used for chemical analysis. Sinter lumps (+10 mm), collected after each test, were used for the Shatter and Tumbling tests. Weight fraction of +10 mm lumps with respect to total weight taken for shatter testing indicated 'Shatter Index' of the sinter sample. Tumbling test was carried out as per IS 3271:1995 standard. In the tumbling test, tumbling and abrasion indices are given by the percentage fraction of +6 mm and -28 mesh sinter, respectively with respect to total sinter mass taken for the test. Phase present in the coarse sinter samples were determined using powder X-ray diffraction method. Selected pieces of the coarse sinter samples were mounted using a cold setting resin, polished and used for microstructural characterisation by optical and scanning electron microscopy (SEM-EDS analysis).

Table 2 : Chemical analysis of the concentrate samples and return sinter

Sample	Chemical analysis, Wt.%								
	Pb	Zn	Fe	Cu	S(total)	S(SO ₄ ²⁻)	C	SiO ₂	AI
Concentrate	41.2	6.51	4.3	2.15	16.6	2.98	4.9	6.5	27.1
Sinter fines	38.0	6.26	16.9	0.42	5.3	1.33	0.5	5.5	8.2

*AI = Acid Insolubles

Table 3 : Summary of sintering conditions used in the tests

Sinter pot grate area = 400 cm²
 Bed height = 300 mm
 Ignition Time = 2 min

Sintering parameter	Test Number							
	1	2	3	4	5	6	7	8
Concentrate, kg	7.20	7.20	7.20	7.20	7.60	7.20	7.20	7.20
Ratio of the concentrate and sinter fines	35:65	35:65	35:65	35:65	40:60	35:65	35:65	35:65
Basicity*	0.85	0.71	0.80	0.80	0.73	0.74	0.76	0.76
CaO (as lime), %	25	40	40	20	40	40	65	65
Iron ore, kg	0.83	0.83	0.83	0.83	1.00	0.80	0.80	0.80
BF slag, kg	0.52	0.52	0.52	0.52	0.60	0.52	0.52	0.52
Water, kg	1.80	1.73	1.76	1.78	1.68	1.74	1.73	1.73
Green mix bulk density, t/m ³	2.52	2.38	2.67	2.46	2.55	2.61	2.74	2.57
Suction, mm WG	560	550	550	550	550	550	550	500

* basicity $\sum_i \text{Wt.}\%(\text{CaO}) / \sum_i \text{Wt.}\%(\text{SiO}_2)$, where i refers to the different constituents in sinter mix.

RESULTS AND DISCUSSION

Sinter Chemistry

The results of chemical analyses of coarse sinter (+10 mm) generated in different tests are compiled in Table 4.

Table 4 : Chemical analysis of sinter samples (+ 10 mm samples)

Element/ Constituent	Chemical analysis of sinter, wt. %							
	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
Pb	36.4	38.7	38.7	38.8	36.6	38.1	37.2	38.5
S _{Total}	0.9	1.0	1.5	1.2	0.9	0.9	0.8	0.8
S/H ₂ S	0.3	0.4	0.8	0.4	0.4	0.3	0.2	0.2
S/SO ₄ ²⁻	0.6	0.6	0.7	0.8	0.5	0.6	0.6	0.6
CaO	7.2	6.0	5.6	6.3	6.3	6.9	7.0	6.7
SiO ₂	9.9	9.9	10.3	9.9	9.2	9.7	9.8	9.5
FeO	24.4	24.2	21.8	21.9	25.1	23.8	24.4	22.8
Cu	0.72	0.73	0.89	0.71	0.76	0.8	0.79	0.78
ZnO	6.6	6.3	6.1	5.8	6.1	5.2	6.2	5.9
C	1.4	1.3	1.8	1.1	1.7	1.1	1.2	0.8

The sulphur content of coarse sinter samples indicates satisfactory sulphur removal in all the tests (much below the 2% limit, mostly ~ 1%) at different substitution levels (20-65%) of limestone by lime and varied sintering conditions as given in Table 3. Close examination of the results indicate that all other conditions remaining same, change in the proportion of the concentrate and sinter fines from 35:65 (Test 6) to 40:60 (Test 5) did not result in any change in S level. Similarly, change in suction from 550 mm (Test 6) to 500 mm (Test 7) did not cause any significant change in S. The results plotted in Fig. 3, indicate following general trends:

- The substitution of limestone by lime remaining fixed, the sulphur content of the +10 mm sinter decreases with an increase in basicity.
- To attain a particular S level with lower amount of replacement of limestone by lime, much higher basicity is required.
- There is an inverse relationship between S level and replacement of limestone by lime. Also, replacement from 40 to 65% does not seem to be as effective as from ~20 to 40%.

It is found that sulphur content of the sinter can be correlated with basicity ($\Sigma_i \text{Wt.}\%(\text{CaO})/\Sigma_i \text{Wt.}\%(\text{SiO}_2)$) and % of limestone replaced by lime (CaOLime, \%) by the following regression equation

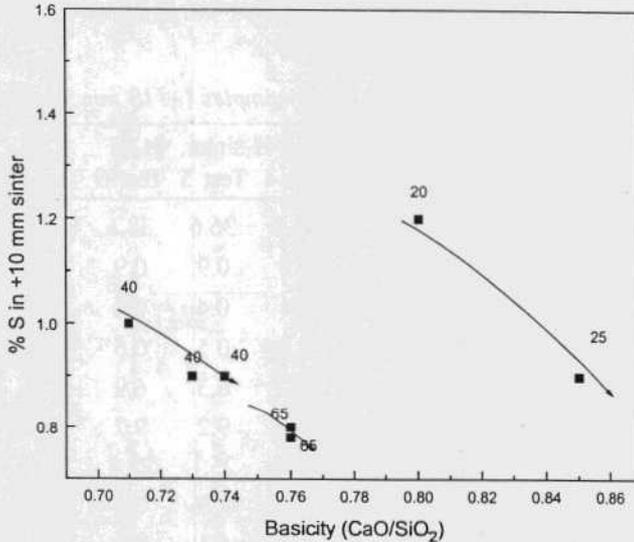


Fig. 3 : Effect of basicity on sulphur content of the sinter at different addition of CaO_{Lime} (CaO_{Lime} (%) indicated on the data points)

Physical Characteristics of the Sinter

The indices of shatter and tumbling signify resistance to breakage after free fall on a hard surface and resistance of the material to breakage or degradation due to tumbling action, respectively. Abrasion index that is complementary to tumbling index and is obtained during the same test, is a relative measure of degradation of the sinter material due to abrasion. Figures 4-6 indicate that substitution of limestone by lime has a beneficial effect on shatter, tumbling and abrasion indices, irrespective of basicity (0.7-0.85) and the ratio of the concentrate and return fines.

Microstructure and Phases

The polished sections of the coarse sinters were examined by reflected light microscopy and SEM-EDS for the assessment of the microstructures formed in the tests. The sinter samples showed a microstructure typical of a good sinter as reported in literature. Microstructure of a bad sinter, that is nonuniform underdeveloped microstructure with unsintered galena, fused region etc was nowhere

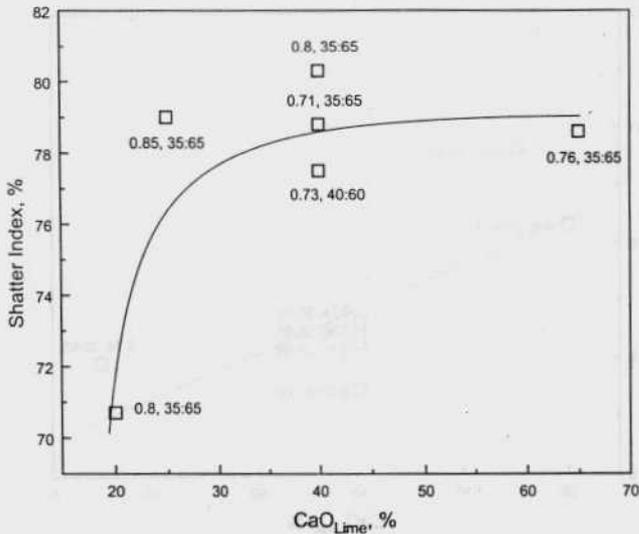


Fig. 4 : Effect of CaO_{Lime} on shatter index of the sinters produced under different experimental conditions (basicity, proportion of concentrate and sinter fines as superimposed on data points)

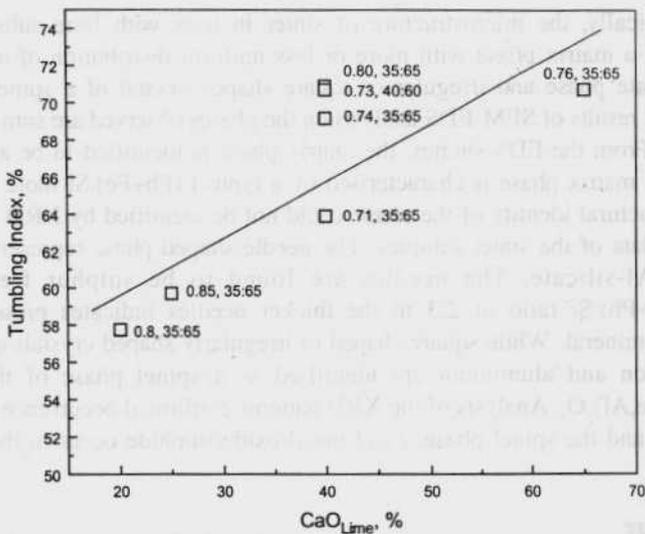


Fig. 5 : Effect of CaO_{Lime} on tumbling index of the sinters produced under different experimental conditions (basicity, proportion of concentrate and sinter fines as superimposed on data points)

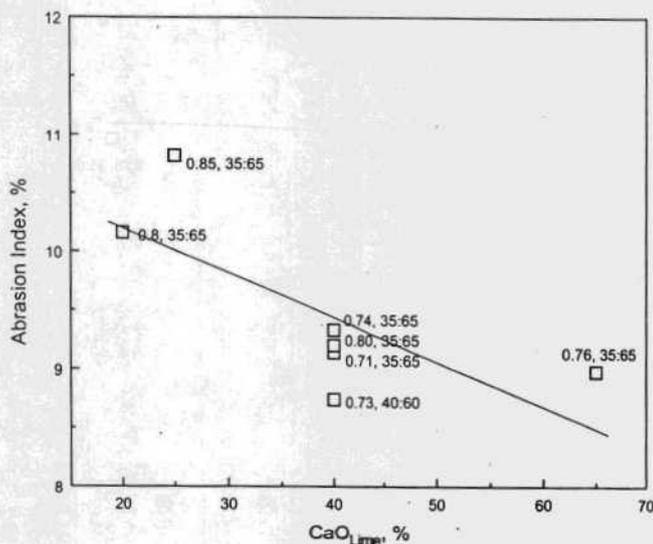


Fig. 6 : Effect of CaO_{Lime} on abrasion index of the sinters produced under different experimental conditions (basicity, proportion of concentrate and sinter fines as superimposed on data points)

visible. Typically, the microstructure of sinter in tests with lime substitution consisted of a matrix phase with more or less uniform distribution of a needle shaped silicate phase and irregular or square shaped crystal of a spinel phase (Fig. 7). The results of SEM-EDS analysis on the phases observed are summarised in Table 5. From the EDS studies, the matrix phase is identified to be a Pb-Fe-silicate. The matrix phase is characterised by a typical (Pb+Fe):Si mole ratio of 3:1. The structural identity of the phase could not be identified by XRD powder diffraction data of the sinter samples. The needle shaped phase represent a Ca-Pb-Zn-Fe-Al-silicate. The needles are found to be sulphur free. The (Ca+Fe+Zn+Pb):Si ratio of 2:3 in the thicker needles indicates presence of hardysonite mineral. White square shaped to irregularly shaped crystals containing zinc, iron and aluminium are identified as a spinel phase of the type $(\text{Fe,Zn})\text{O} \cdot (\text{Fe,Al})_2\text{O}_3$. Analysis of the XRD patterns confirmed occurrence of both hardysonite and the spinel phase. Lead metal/oxide/sulphide occur in the sinter only rarely.

Role of Lime

The presence of lime inhibits the early formation of low melting phase that results in non-uniform sintering. Use of lime favours the formation of phases that are required for a good sinter. Beneficial effect of lime in iron ore sintering has

been reported^[9]. However, information on lead sulphide ore sintering is scarce. Some relevant facts pertaining to lime usage in sintering^[9] and their likely implications in the present case are presented here to provide a possible explanation for the observed beneficial effect of lime:

- During mixing and moistening, lime added as CaO into the sintering mixture forms calcium hydroxide (Ca(OH)₂). The hydration is accompanied by volume expansion resulting in the formation of finely dispersed particles that can improve pelletability and gas permeability of the mixture.
- Lime slacking is accompanied by liberation of heat (4.214 kcal/kg of CaO) and consequent rise in the temperature of the sinter mix that help in the intensification of the sintering process.
- An intense absorption of moisture by lime due to hydration can reduce the mixture over-moistening in sintering. It is likely to have a beneficial effect in controlling breakage of the sinter structure and maintaining sinter bed permeability. This is especially going to be important since the used concentrate has a fine granulometry.
- Lime can activate carbon and increase its reactivity or combustion rate.

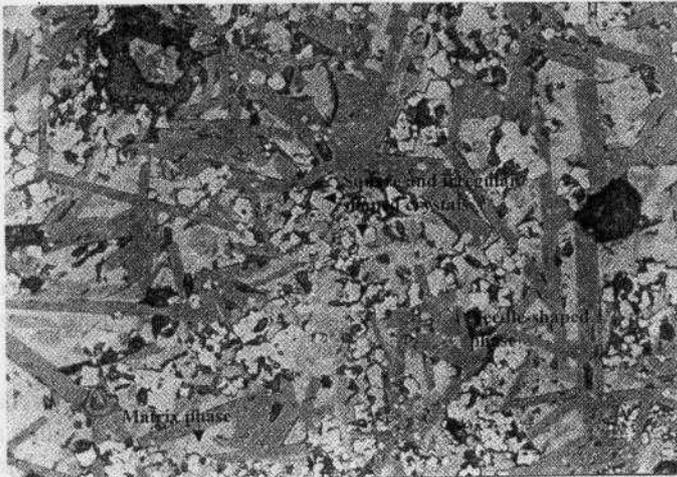


Fig. 7 : Optical micrograph showing typical microstructural features present in the sinter samples after lime addition.

Table 5 : SEM-EDS analysis of major phases in Fig. 7

Element	Weight %	Atomic %
Lead silicate matrix phase		
Si	4-6	20-24
S	0-4*	0-8
Fe	7-16	16-32
Cu	0-5*	0-11
Pb	78-86	44-54
Needle shaped phase		
Al	0-3	0-4.5
Si	27-29	40-42
Ca	42-45	44-45
Fe	1.5-4	1-2.5
Zn	12-17	7-12
Pb	8-10	1-2
Square or irregular shaped crystals		
Al	0-4.5	0-9.1
Fe	68-79	76-78
Zn	17-28	14-25

* mostly absent

CONCLUSION

Following are the major conclusions that follow from the study:

1. The problem of bad sinter formation due to use of the low-grade complex concentrate with fine granulometry can be tackled by adding lime to the sinter charge mix as part replacement of limestone.
2. Good sinter with desired sulphur content and microstructure is produced in the tests that were carried out with wide variation in CaO addition as lime (20-65% of total CaO), basicity (0.72-0.85), proportion of concentrate and sinter fines (RD Concentrate:Fines - 35:65 to 40:65) and suction (500-560 mm for 30 cm bed height).
3. To overcome the problem of bad sinter, the optimum level of lime addition is about 40% of the total CaO addition to the sinter.

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