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A Microscopy Study of Lead Sinter

T. J. O'KEEFE, C. BENNETT, AND E. R. COLE

Samples of up-draft sinters produced at three different Missouri lead smelters were studied, to determine the chemical phases present, as a first step toward a more complete understanding of the lead blast furnace operation. The sinters seemed to be basically similar, and all the results reported are from samples from one smelter (Herculaneum smelter, St. Joe Minerals). Analytical tools used included the electron microprobe and scanning electron microscope with a non-dispersive X-ray spectrometer attachment. Major phases that were positively identified are metallic lead, lead sulfide and zinc ferrite. The predominant lead phase was tentatively identified as a lead oxide-silicate compound. Other compounds probably present are calcium, iron, zinc-silicates or some combination of calcium, iron or zinc with silica. Contrary to the results of other investigators no lead oxide or basic lead sulfate compounds were identified. It appears that the majority of the lead is present in the sinter as a lead oxide-silicate phase.

THE important effects which sinter practice and quality have on smelting efficiency have long been recognized. But due to the physical and chemical complexity of lead sintering it has proven to be a difficult task to establish just what constitutes a good sinter. A number of experimental studies and theoretical analyses have been made over the years on the physical chemistry of the Pb-S-O system.¹⁻⁴ The results of these experiments are very helpful in gaining an understanding of a number of phenomena observed during the thermal processing of lead ores but there are certain restrictions and limitations on their use. Since most of these studies were essentially equilibrium type investigations they would be of questionable value in predicting phase relationships obtained during blast roasting. Also the chemistry of the experimental investigations was less involved than that encountered in actual practice. Lab sintering work and plant scale studies have also been performed^{5,6} using systems more comparable to those found in a commercial process. However, primary emphasis was placed on physical parameters as a guide to sinter quality. The bulk quantitative chemical analysis of the sinter has also been well defined, but surprisingly there have been only limited attempts to characterize the constitution of the sinter. Since it was felt that specific phase information would be necessary before a more meaningful understanding of the sintering process could be gained, numerous samples of commercial sinter were studied in an effort to identify the nature of lead sinter from a chemical constitution viewpoint.

EXPERIMENTAL PROCEDURE

All of the sinter samples used for the phase identification portion of this work were obtained from the Herculaneum Lead Smelter of the St. Joe Minerals Corp. Metallographic studies were also made on sinter samples from the Bulck smelter of Amax-Home-stake and the Glover smelter of Asarco, and the struc-

ture of these samples was found to be very similar to the structure of the samples from the Herculaneum smelter. All of the sinter used in this investigation was produced on a Dwight-Lloyd up-draft sinter machine. A detailed description of the sintering process has been given previously.⁷ The specimens studied were taken at random from the samples of finish sinter used for routine chemical analysis by the plant. Since preliminary results indicated a similarity in the make-up of the sinter, extensive phase analyses were made on only four different specimens. These pieces were selected from various sized chunks of original sinter and the time span over which the different samples were produced was about 3 months. The broad base used in selecting samples was felt to be necessary due to the differences noted in the physical appearance of sinter produced at different times. It was found upon investigation, however, that the chemical phases in the various sinter samples remained fairly constant even though their relative concentration, size, morphology and general physical appearance did change with variations in the sinter process.

The structure of the sinter was determined by metallographic and scanning electron microscopy techniques. Standard polishing procedures were used and none of the samples were etched. Attempts were also made to identify the phases present using both X-ray diffraction and Debye-Scherrer film patterns. The bulk of the X-ray work was done with Cu and Fe radiation, but a few patterns were made using Co radiation. Quantitative analyses were made on the individual phases using an electron microprobe and qualitative analyses were also made with a non-dispersive X-ray spectrometer in conjunction with the scanning electron microscope (SEM).

RESULTS

Metallography and Microscopy

Prior to formally studying the sinter, some preliminary attempts were made to separate the material by various physical and chemical treatments. It was found that the sinter was strongly magnetic, even when crushed to -325 mesh. However, the magnetic phase was so finely disseminated throughout the entire sinter that it was virtually impossible to separate it.

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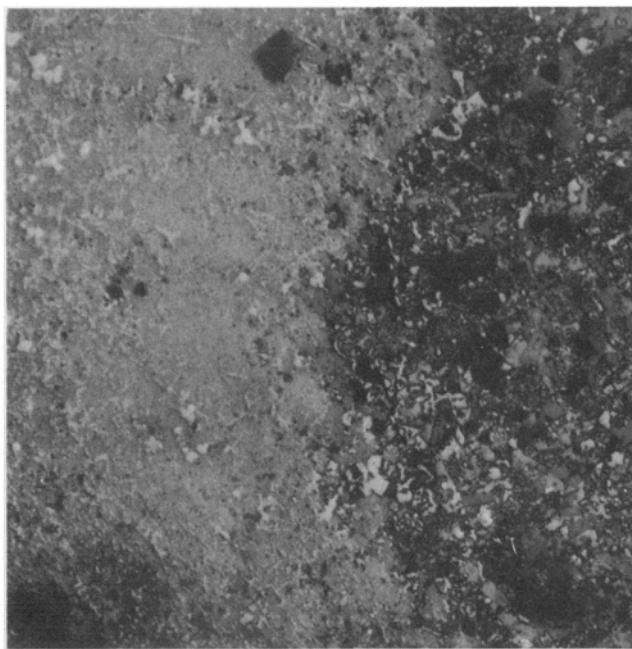


Fig. 1—The two predominant phases detected in the lead sinter. The light gray "A" phase is at the left and the darker "B" phase is at the right. Magnification 200 times.

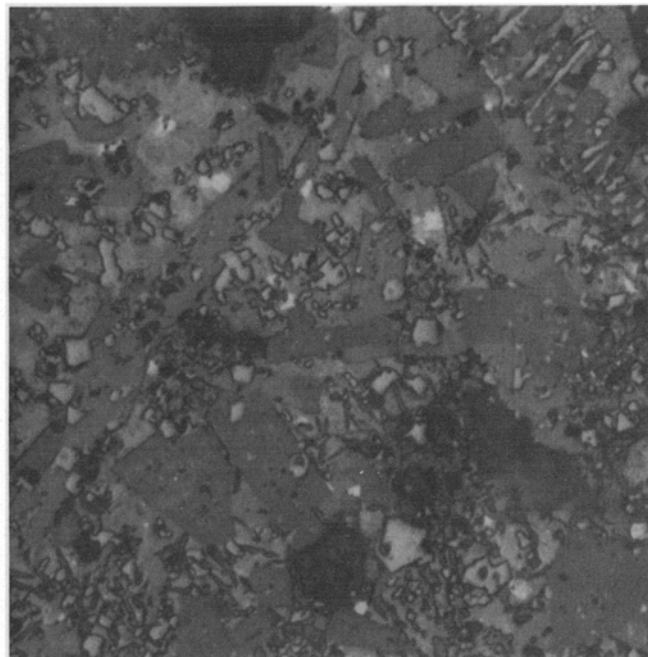


Fig. 3—The "B" phase showing the light gray matrix "B-1" and darker, block-like "B-2" phases with smaller, light colored "B-3" phase dispersed throughout. Magnification 500 times.

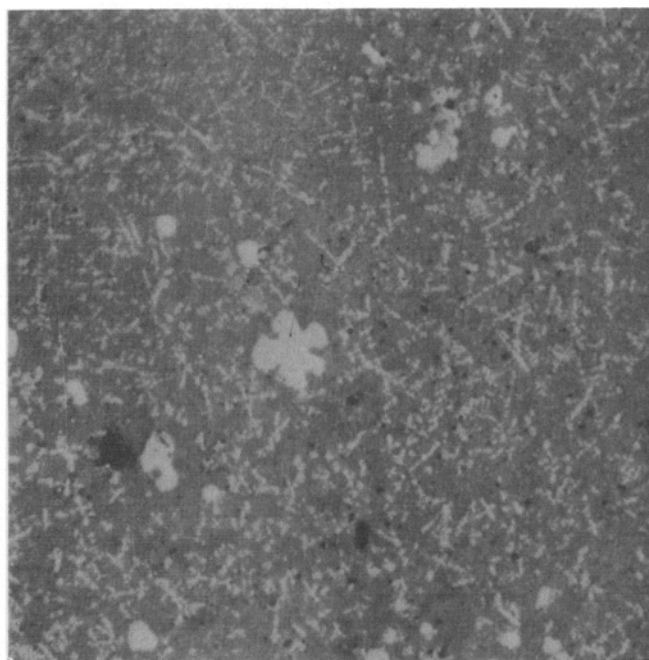


Fig. 2—The "A" phase showing the gray matrix "A-1" and light colored dendritic "A-2" phases. Magnification 500 times.

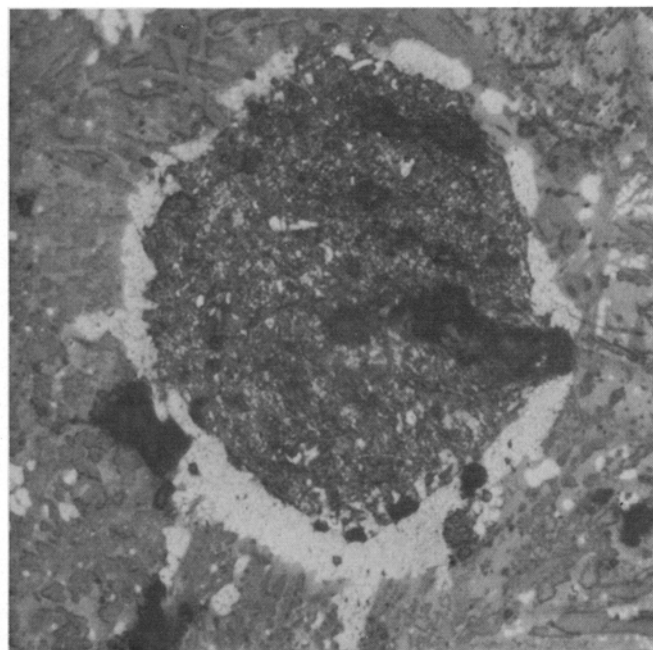


Fig. 4—Rounded "C" phase particle surrounded by the "D" phase. Magnification 500 times.

The microscopy results indicated that in spite of the complexity of the sinter, four predominant phases comprised the majority of the materials. The bulk phases were found to vary slightly in chemistry or morphology, but most likely this was a result of the particular process conditions. Thus, it appeared that the basic make-up of the sinter could be characterized, and that no extreme variations in phases occurred from sample to sample. Closer examination revealed that at least two of these four bulk phases were not homogeneous and actually were a combination of two

or more separate and distinguishable chemical compounds. The two major phases are shown in Fig. 1 at a low magnification, while Figs. 2 and 3 show these same phases at a higher magnification. The lighter of the two phases in Fig. 1, or shown more clearly in Fig. 2, was called the "A" phase. The darker phase of Fig. 1, which is also shown at higher magnification in Fig. 3 was called the "B" phase. The other two phases detected, which were found randomly distributed throughout the sinter are shown in Fig. 4. The darker, round particle was termed the "C" phase,

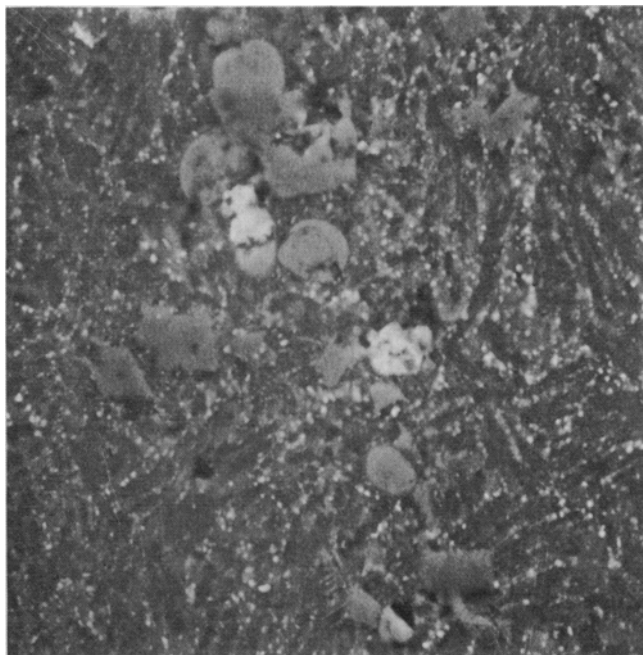


Fig. 5—SEM micrograph of the "A" phases. Magnification 1000 times.

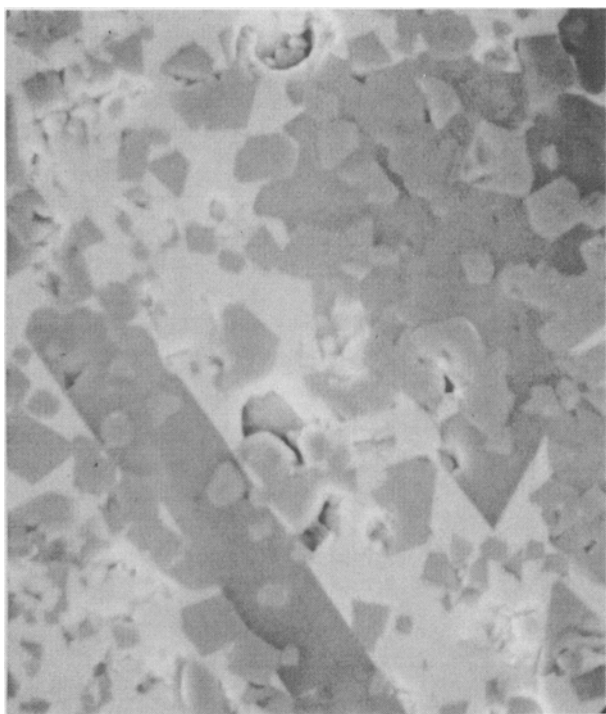


Fig. 6—SEM micrograph of the "B" phases. Magnification 1000 times.

while the lighter phase surrounding it was called the "D" phase. These designations will be used to identify the phases in the subsequent sections. As mentioned previously, the physical appearance of these phases would vary. This can be seen in Figs. 2 and 5 which show the "A" phase from two different samples. In one case there is a very dendritic pattern (Fig. 2) for one of the phases which is not the case with the other sample (Fig. 5). Sometimes the relative sizes of the different chemical compounds in the

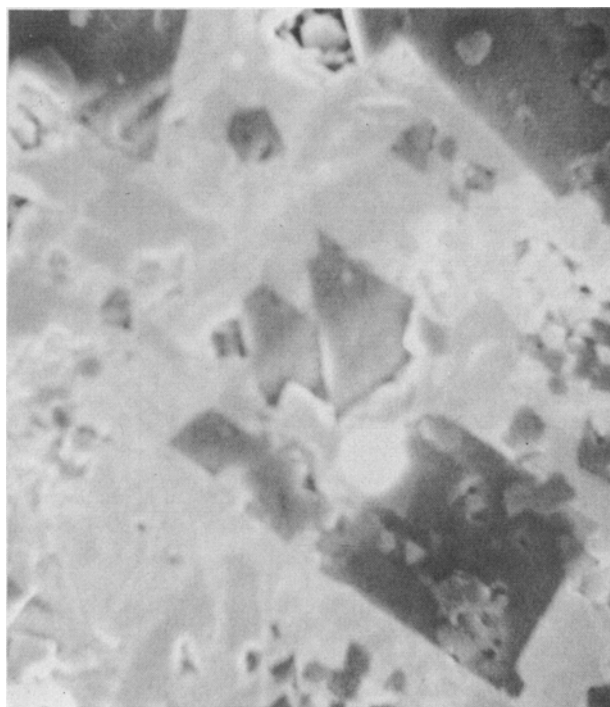


Fig. 7—SEM micrograph revealing indications that the light gray "B" phase may be of variable composition. Magnification 1000 times.

"B" phase were also quite different. In some, the structure was more massive with a definite degree of angularity in evidence. Even with these variations, however, their relative chemical compositions remained constant. Fig. 6 shows "B" phase in greater detail (1000X). There were always some traces of other phases such as calcium sulfate or potassium-aluminum-silicates which were present in the various samples in addition to the four basic phases. These two phases were never found in any substantial quantity and were most likely associated with certain impurities introduced with the slag, fluxes, etc. It is not to be intimated that identification or importance of these is to be overlooked, as they may play a major role in determining sinter quality. However, it was felt that a more controlled experiment on the production of the sinter would be necessary to make such a detailed study justified.

The lead sinter was thus found to consist of four predominant phases. The "A" phase was a dark, slag-like material apparently consisting of two different chemical compounds. The one compound was lighter in color and appeared with either a dendritic or a block-shaped structure. The darker matrix was assumed to be a single compound, but in some cases it looked as though it might be a mixture of two or more very finely divided compounds.

The "B" phase was found to contain at least three distinguishable compounds, and in some instances possibly four. The matrix, as seen from the micrographs, was composed of two rectangularly shaped phases, one substantially darker than the other. A very sharp definable interface usually existed between the two. In some cases it seemed that the lighter appearing compound was made up of two materials with slightly different shades of gray and was not truly a

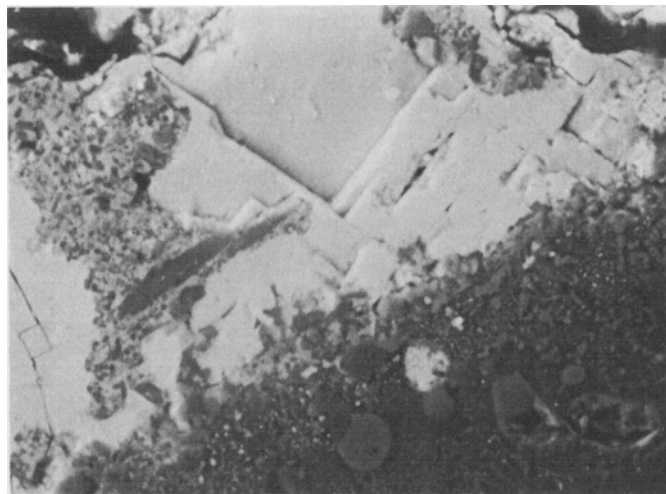


Fig. 8—SEM micrograph of the "D" phase showing cubic type cleavage. Magnification 600 times.

single phase. This phase actually had more of a green-gray appearance under the light microscope. This is more evident as seen in Fig. 7 which shows an SEM photo of the "B" phase at 1000X. In making a quantitative analysis of this phase it was assumed that this lighter portion of the "B" phase was one homogeneous material. If this proves to be incorrect the reported analyses probably represents an average chemical composition. A third material, which had very sharp features and was block shaped, was found to be uniformly distributed throughout the "B" phase. This material had the same general appearance as the finely divided compound seen in the "A" phase.

The "C" phase had a metallic appearance and was found to oxidize rather quickly after polishing. This portion of the sinter seemed to be a single phase. The "D" phase also appeared to contain only one compound, and when viewed at higher magnifications (600X) on the SEM the material seemed to be rather brittle and showed a cubic type cleavage (Fig. 8).

Microprobe Analyses

Once the specific phases present in the sinter had been categorized, attempts were made to determine the chemical analysis of each using an electron microprobe and also a non-dispersive X-ray spectrometer which was attached to the SEM. The main elements found in the phases were Pb, Fe, Zn, Si, S, and Ca. There were always some traces of other elements such as K, Al, Ti, Co, Mg, Cu, and so forth, but these

will not be reported. The exact oxygen content of each was also not determined, as it was very difficult to detect oxygen in the presence of such a high Pb concentration.

The high lead content also appeared to be the reason that a 100 pct accountability could not be obtained in all phases. Therefore, in low Pb containing phases, where only about 60 to 70 pct of the phase can be accounted for, it is assumed that the individual elements are in the proper ratios but the indicated weight percentages are less than actually present. The microprobe results are shown for four different samples. An average figure could have been determined, but it was felt that this might be misleading. It is also apparent from the metallography that some variations in results would be expected because the individual compounds are so finely divided in some cases. This made an exact placement of the electron beam very difficult and a slight overlap onto different surrounding materials could easily have occurred.

The microprobe results are given in Table I.

A zero indicates a value of less than 1 pct by weight. It can be seen that the "A-1" or matrix phase is either a complex Ca, Fe, Zn-silicate or possibly two separate compounds such as a CaFe- and CaZn silicate. It was interesting to note that the Pb content of the phase was in a range similar to that encountered in normal blast furnace slag. The "A-1" material (the dendritic phase or block phase) seems to be a high Fe content zinc-ferrite. Some Pb was always detected in this phase, but it could have been due to beam overlap as previously mentioned. Although it is not listed in the table, Al was commonly present in the "A-2" compound also.

The "B" phase is seen to be divided into "B-1," "B-2," and "B-3" components. The light colored "B-1" phase was highest in Pb content, with definite quantities of Si also being detected. It was therefore assumed that the predominate phase was not a pure lead oxide, but rather a low silicate phase (such as $4\text{PbO}\cdot\text{SiO}_2$). The "B-2" phase always had a fairly high lead content, but was basically a (Ca, Zn) silicate. The "B-3" phase is not shown in the tables as the analyses were identical with the "A-2" phase and was also a high Fe content Zn ferrite. This was not surprising since there should have been a magnetic material present in all of the major components, as per the magnetic tests. The "C" phase is not listed, but it was found to be metallic lead containing minor amounts of impurities (S, Cu, etc.). The "D" phase surrounding Pb was almost stoichiometric PbS. The cubic cleavage exhibited in the metallographic specimen (Fig. 8) also tended to confirm this.

Table I. Microprobe Analyses of Phases in Lead Sinter Wt Pct

	A Phase								B Phase								D Phase			
	A-1				A-2				B-1				B-2				D-1			
	H-8	H-29	H-52	H-71	H-8	H-29	H-52	H-71	H-8	H-29	H-52	H-71	H-8	H-29	H-52	H-71	H-8	H-29	H-52	H-71
Fe	18	18	11	22	49	41	37	45	1	4	2	2	2	1	1	1	0	0	0	0
Zn	11	12	11	14	14	12	18	15	1	3	5	2	9	8	7	9	0	0	1	0
Si	7	6	9	6	0	1	0	0	4	3	4	5	9	11	9	13	0	0	0	0
S	1	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	13	11	13	12
Pb	4	2	7	5	1	1	1	1	64	61	64	62	8	6	6	8	75	67	77	84
Ca	10	8	6	6	1	1	0	0	1	1	0	2	11	16	12	12	0	1	0	0
	51	47	44	54	64	56	56	61	71	72	75	73	39	42	35	43	88	79	91	96

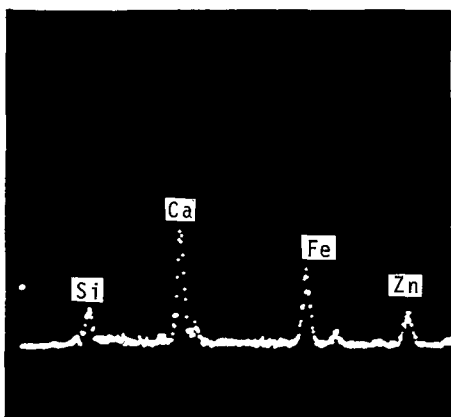


Fig. 9—Elemental analysis of "A-1" phase.

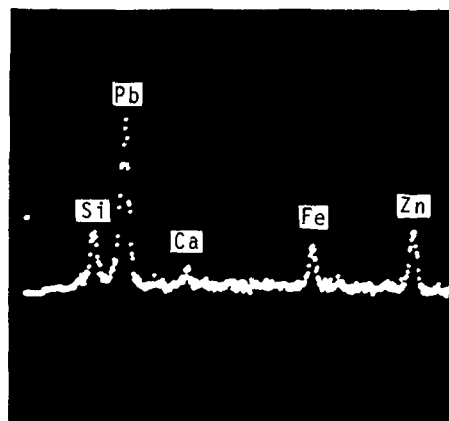


Fig. 12—Elemental analysis of "B-1," dark phase.

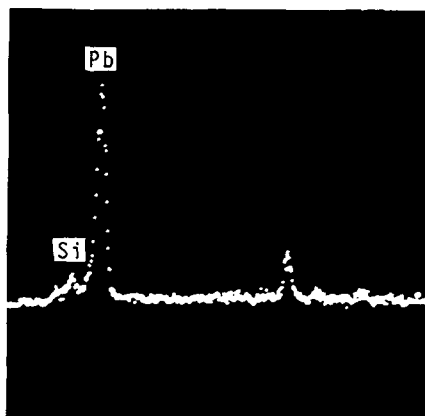


Fig. 10—Elemental analysis of "B-1," light phase.

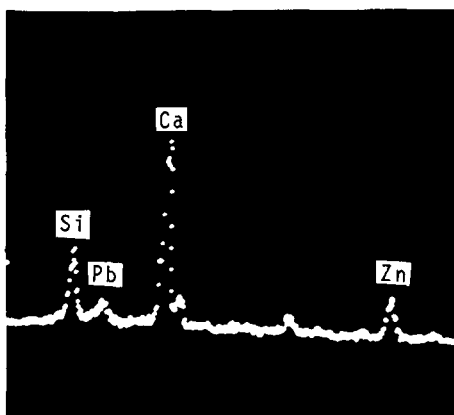


Fig. 11—Elemental analysis of "B-2" phase.

There was no evidence of any phase which would correspond to a basic lead sulfate. At times there were heavily oxidized layers on the outside portions of the sinter, but these were not studied.

Selected areas from the samples were also scanned using a non-dispersive X-ray spectrometer. Since this analytical unit was used in conjunction with the

SEM it was possible to focus on much finer areas than with the microprobe. The results are not as good from a quantitative standpoint, so only the more qualitative aspects of the results should be used. Fig. 9 is of area "A-1" while Figs. 10 and 11 are of the "B-1" and "B-2" regions. At the higher magnifications it was possible to distinguish two separate materials in the "B-1" phase. The analysis of the darker of the two is shown in Fig. 12. This is obviously higher in Si, Zn, etc., than the lighter region adjacent to it. It was not possible to properly analyze these two finely divided phases on the microprobe initially, but attempts are now being made to overcome the physical difficulties encountered. Overall, the non-dispersive X-ray results tended to confirm the results obtained on the probe. They also pointed out, however, some of the problems in accurately defining the exact chemical composition of such complex, finely divided materials. This also probably accounts for at least some of the variations found for apparently the same phase when analyzed in different samples. The ranges of chemical compositions of the sinters used in this work are listed in Table II.

X-ray Diffraction

An X-ray diffraction pattern, which was representative of the average sinter sample is given in Table III. It was possible to account for most of the stronger lines, but as is often the case with complex samples, there were a number of discrepancies. A part of the problem was probably due to the manner in which the phases were formed. It is quite likely that there is no exact duplicate in the ASTM card index to correspond to some of the phases in the sinter, particularly the silicates.

A positive identification was made for Zn-ferrite, PbS, and Pb. The identifications of the remaining phases are quite tentative, and are based primarily on the approximate compositions obtained from the

Table II. Chemical Analyses of Sinter Samples*

Total Lead	Cu	SiO ₂	FeO	CaO	MgO	Total S	Zn	Al ₂ O ₃	Estimated	
									Metallic Pb	Sulfate S
43.4-50.8	0.5-0.9	8.1-10.9	14.3-18.0	4.7-5.7	1.9-2.6	1.0-1.6	6.5-8.2	1.5-1.7	5.3-17.7	0.6-0.8

*All analyses performed by the St. Joseph Minerals Co., Herculaneum, Mo.

Table III. Lead Sinter Cu Radiation Ni Filter

I	θ (deg)	Sin θ	d Å
VW	9.107	0.1583	4.870*
VW	10.564	0.1833	4.206
VW	12.188	0.2112	3.650
VW	13.068	0.2261	3.410
M	14.575	0.2517	3.063
M	15.204	0.2622	2.940*
M	15.731	0.2711	2.844
VW	17.239	0.2964	2.601
S	17.867	0.3069	2.512*
VW	20.365	0.3481	2.215
M	21.687	0.3696	2.086*
VW	22.366	0.3806	2.025
VW	23.396	0.3971	1.941
W	24.602	0.4163	1.852
VW	25.633	0.4326	1.782
VW	26.085	0.4398	1.753
W	26.814	0.4510	1.709*
VW	27.301	0.4586	1.681
M	28.648	0.4795	1.608*
VW	29.965	0.4995	1.543
S	31.463	0.5219	1.477*
VW	32.780	0.5414	1.424
VW	33.483	0.5516	1.398
VW	35.695	0.5835	1.321*
VW	37.202	0.6046	1.275*
VW	39.766	0.6397	1.205*
VW	43.686	0.6908	1.116*
W	45.093	0.7082	1.089*
VW	47.355	0.7356	1.048*
VW	51.326	0.7808	0.987*
W	52.833	0.7968	0.967*
VW	55.497	0.8241	0.935*
VW	61.553	0.8792	0.877*
W	64.292	0.9010	0.856*

*Zinc ferrite.

microprobe results. There were relatively strong indications that a zincian melilite $\text{Ca}_2(\text{Zn, Fe})\text{Si}_2\text{O}_7$ or $\text{Ca}_2\text{ZnSi}_2\text{O}_7$,⁸ type phase was also present. The same could be said for a phase of the type $\text{Ca}_3\text{Si}_2\text{O}_7$, but again definite identification was not possible. No strong evidence for either a PbO or a basic lead sulfate phase was found in the X-ray patterns. Some of the necessary peaks were present, but comparisons between the sinter pattern and those for pure Pb oxide phases indicated the Pb was not in the form of a pure oxide. Since this was also borne out by the microprobe results, it appears that the predominant lead phase is a low silicate, possibly of the type $4\text{PbO}\cdot\text{SiO}_2$.

Four basic phases were found to be common to the lead sinters from three different Missouri lead smelters. Two of these four phases were positively identified as metallic lead and lead sulfide. Of the remaining two basic phases, one was a slag like phase containing a high iron content zinc ferrite and a Ca, Fe, Zn-silicate compound of undetermined stoichiometry. The fourth phase contained the majority of the lead as a low silicate compound of the type $4\text{PbO}\cdot\text{SiO}_2$. No evidence of a pure lead oxide compound was found. The fourth phase also contained a high iron content zinc ferrite and a (Ca, Zn) silicate compound.

CONCLUSIONS

The results of this study tend to confirm a number of things which were thought to be true of lead sinter,

but seem contradictory to a number of other previously held beliefs. The main differences seem to stem from conclusions about sinter composition which were made from results of equilibrium studies on systems similar to those encountered in lead sintering, but of less chemical complexity. Specifically, there does not seem to be any evidence of a basic lead sulfate phase present in any of the samples studied. Some small amounts of a lead sulfate phase could have been overlooked due to the small amount of total sulfate present, but there was probably a sufficient amount of calcium sulfate detected to account for most of it. Also, there does not seem to be any compound consisting of only lead and oxygen. Of course, some PbO was found on the outer surfaces of the sinter which were exposed directly to the air, but never found internally in the sinter. Certainly more work is required in many of the areas investigated, but at least the initial results show some of the phases to be quite different than normally assumed. The manner in which a substantial portion of the sulfur is combined was also unexpected. The presence of PbS in conjunction with metallic lead, rather than being more uniformly distributed as unreacted galena, sheds a different light on the possible means of increasing sulfur elimination during roasting. Obviously this aspect also deserves additional attention. The highly magnetic nature of the sinter and the distribution of the zinc ferrite throughout could also be of importance, particularly from the standpoint of sinter strength. Examination of the micrographs indicates that the fine ferrite particles are acting in a manner similar to an oxide dispersed material. The fact that the highest lead phase was a low silicate is probably not too surprising considering the finely divided nature of the original charge and the proximity of such quantities of high silica containing materials.

Overall it appears that a knowledge of the phase morphology and distribution could be most helpful in attempting to control the subsequent reduction step. It is however, still a relatively complex operation and more fundamental studies will be required before it can become a reality.

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