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Constitution and Specific Gravity of the Ternary Mattes Cu_2S-FeS-PbS.

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SENIOR THESIS

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Inaugural Thesis

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The constitution of the ternary mattes Cu_2S-FeS-PbS has never been completely investigated. Fulton and Goodner 1) have investigated the binary mattes Cu_2S-FeS, Cu_2S-PbS, PbS-FeS and have shown that the three binaries show eutectics. There has been no attempt however to draw the complete ternary diagram. The following work is intended to be a contribution toward the completion of this diagram by first of all pointing out those mattes which separate on melting into two layers, and second by determining the specific gravities of mattes of different compositions.

Procedure

The mattes of various compositions were obtained by melting together the correct proportions of the three components, Cu_2S, FeS and PbS. The Cu_2S used was in the form of chalcocite, the PbS in the form of galena, and the FeS used was that commonly employed in the generation of H_2S gas. These three components were ground to pass through a 100 mesh screen, were thoroughly mixed on a rolling cloth and then placed in a Corrs porcelain crucible.

Annealing cups and fire clay crucibles, even though brasqued were found to be unsatisfactory as at the temperatures employed, the molten matte soaked through almost

1) Fulton & Goodner: Tr. A. I. M. M. E. 39, (1908) 584.

completely, and due to the high corrosive action of the mattes on iron, crucibles of this metal were also unsatisfactory.

Charges varying from 12½ grams each for the binary mixtures to 20 grams for the ternary mixtures were used, a layer of Dixon's graphite was placed over the mixture and an iron lid placed over the crucible to prevent oxidation. In spite of these precautions some oxidation did take place, due to the air already inclosed in the mixture. This oxidation is evidenced by the appearance of microscopic particles of metallic copper and lead in the mattes, visible however only under the microscope. The occurrence of the copper was due to an oxidation which proceeded according to the following chemical reactions:

$$2\ Cu_2S + 3\ O_2 \rightarrow 2\ CuO + 2\ SO_2$$

$$Cu_2S + 2\ CuO \rightarrow 4\ Cu + SO_2$$

Metallic lead was produced according to similar reactions:

$$2\ PbS + 3\ O_2 \rightarrow 2\ PbO + 2\ SO_2$$

$$2\ PbO + PbS \rightarrow 3\ Pb + SO_2$$

The occurrence of these metallic particles was not frequent nor voluminess enough to affect materially the specific gravity of the resulting mattes. The melting took place in an oil fired muffle furnace and the molten mixtures were held at 1400° C for from 2 to 3 hours. They were then allowed to

cool in the furnace, removed, and the porcelain crucibles broken away.

The Constitution of the Mattes

A complete thermal analysis of the various mattes was not attempted but the macroscopic and microscopic examinations revealed some interesting results, regarding the possible miscibility of the components one in another. For example, all of the mixtures of the binaries Cu_2S-FeS and FeS-PbS appeared homogeneous to the eye, whereas all of the mixtures studied in the Cu_2S-PbS series solidified in two layers. This solidification in two layers was noted also in all of the ternary alloys lying close to the Cu_2S-PbS side of the equilateral triangle. Examples of such separation are shown in Fig. 1 and Fig. 2.

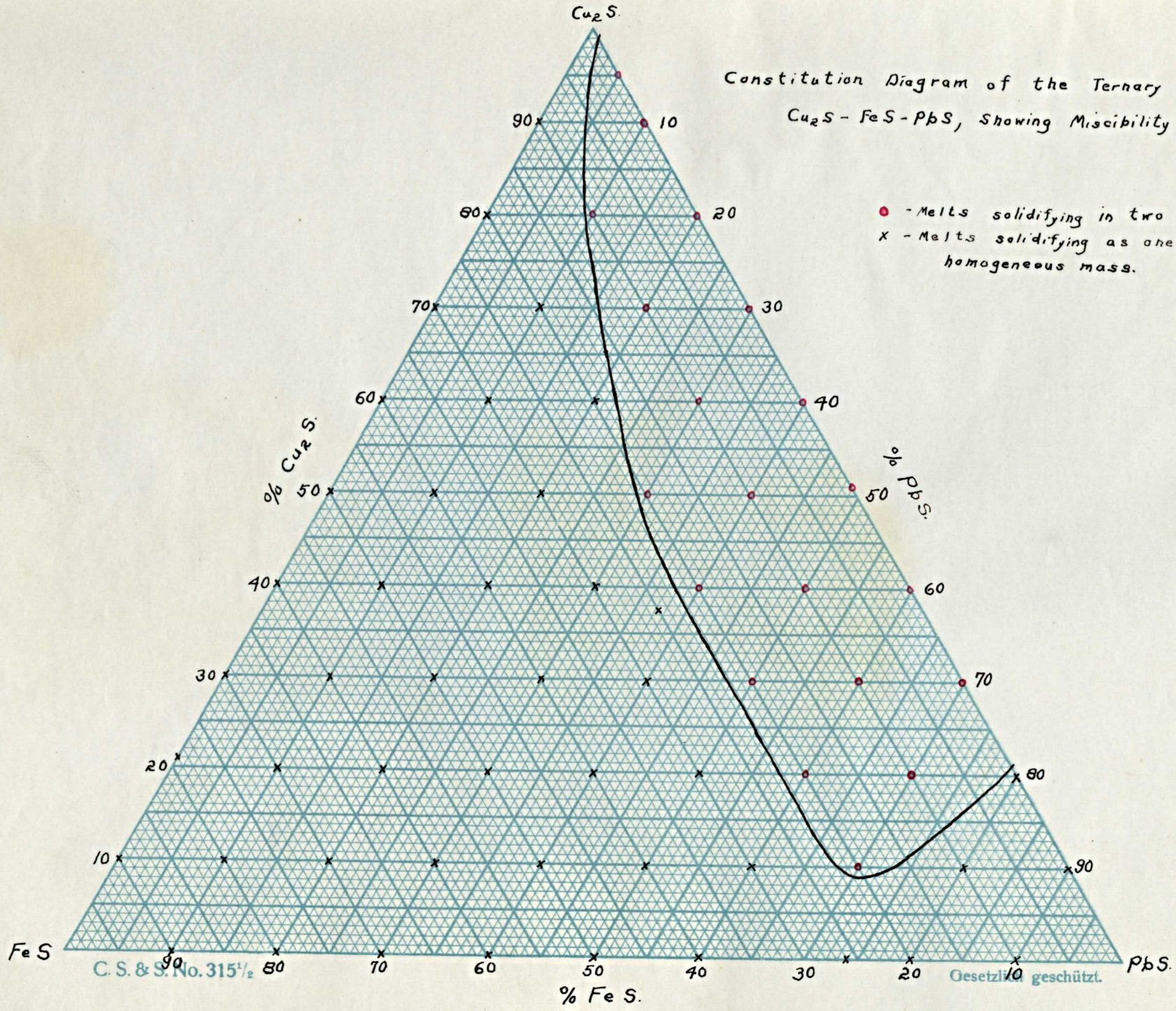
Fig. 1

Fig. 1 shows a matte containing 80 % Cu_2S, and 20 % PbS, magnified four times.

Fig. 2.

Fig. 2 shows the roughly polished section of a matte containing 70 % Cu_2S, 10 % FeS, and 20 % PbS, magnified four times. These two mattes were representative of all those separating into two layers.

Fresh charges were melted and these melts confirmed the results of previous tests. Fig. 3 shows those mixtures which separated into two layers and those mixtures which solidified as a seemingly homogeneous mass. It was at first thought that this solidification into two layers indicated



an immiscibility in the Cu_2S rich and PbS rich layers but the chemical analysis of the separate layers of several of the mixtures showed that each layer contained at least one of the components in exactly that proportion which was originally introduced into the melt. The results of analyses are tabulated in Table I.

Table I.

Partial analysis of layers of matte bottons.

Layer	Components introduced, in %		Analysis
	Cu_2S	PbS	
Bottom	10	90	Cu - 8.0 % = Cu_2S - 10.0 %
"	30	70	Cu - 23.87% = Cu_2S - 29.8 %
"	80	20	Pb - 16.9 % = PbS - 20.0 %
Top	90	10	Pb - 8.2 % = PbS - 9.8 %

Copper was estimated by KCN method and lead by molybdate method of analysis.

Furthermore, microscopic examination of polished sections of the mattes showed very definite eutectics in both the layers; these are shown in the accompanying photomicrograph in Fig. 4. Peter's [1] mentions that Röntgen observed this same occurrence of two layers in the Cu_2S-FeS series, the composition of the two layers being practically the same. In the present investi-

1) Peter's - Principles of Copper Smelting--pp. 411-413.

gation none of the Cu_2S-FeS series exhibited this separation and all of the two layer mattes were limited to the area indicated in Fig. 1.

Fig. 4.

Photomicrograph showing the eutectic mixture of Cu_2S-PbS, Cu_2S - 51 % and PbS - 49 %.

The Specific Gravity

The specific gravity of the mattes was determined by means of a pycnometer, using about three grams of the matte broken to particles the size of a pea. Occasionally a vesicular structure was noticed and in these cases it was

necessary to take portions of the matte which were completely solid. The specific gravity was then calculated from the formula:

$$\text{Density of solid} = \frac{a\ d}{b - c - a}$$

where

a = weight of solid

b = weight of pycnometer and water.

c = weight of pycnometer, water, and solid.

d = density of water.

The resulting specific gravities are tabulated in Table II. and indicated graphically in Fig. 5. It is to be noted that in the case of those mattes which had two layers the specific gravity of the bottom layer in each case was taken, as this layer appeared more homogeneous.

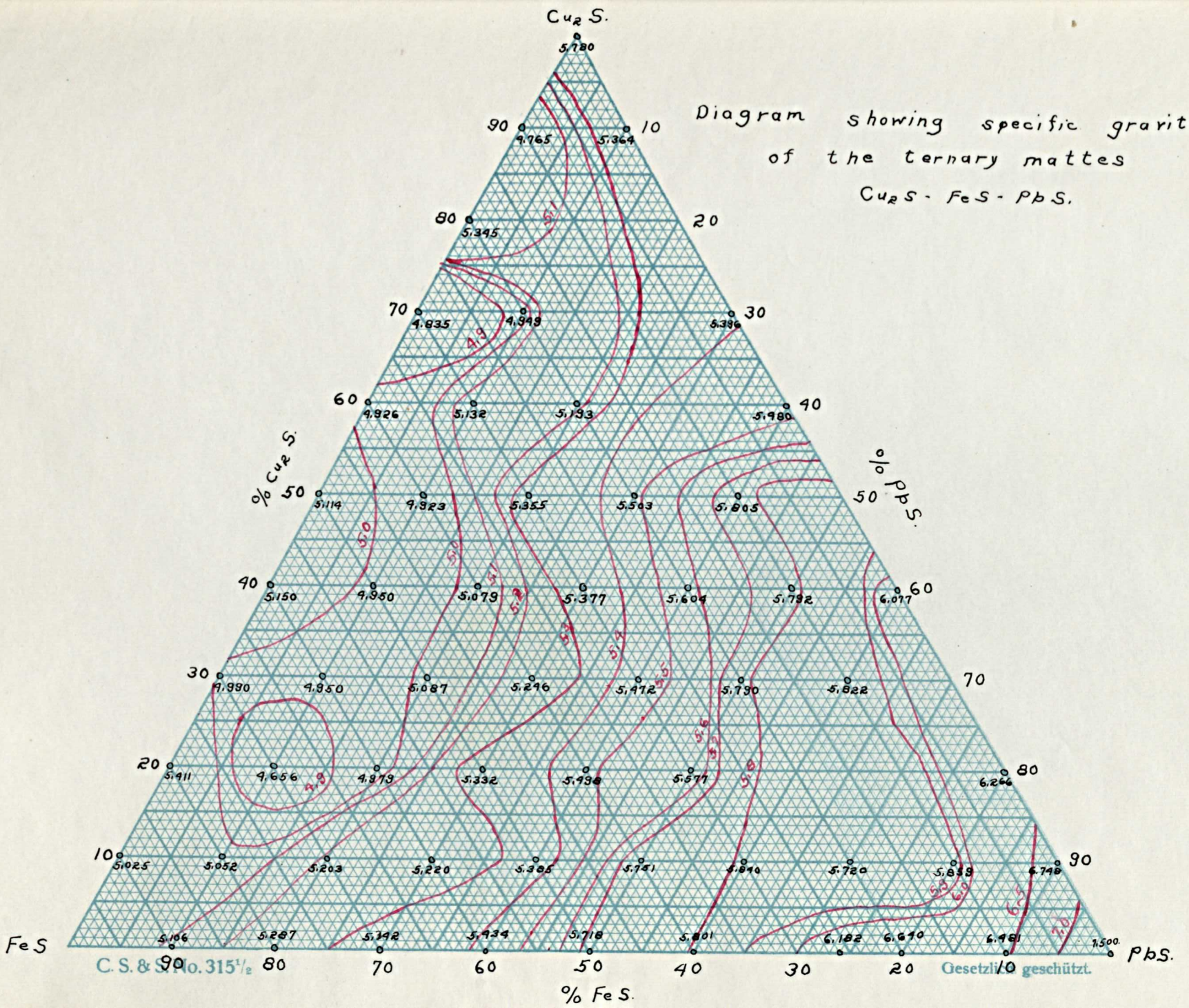


Table II.

The Specific Gravities of the ternary Mattes Cu_2S-FeS-PbS

A. The binaries Cu_2S-FeS

Composition in %		Specific Gravity
Cu_2S	FeS	
10	90	5.025
20	80	5.411
30	70	4.990
40	60	5.150
50	50	5.114
60	40	4.926
70	30	4.835
80	20	5.345
90	10	4.765

B. The binaries Cu_2S-PbS

Composition in %		Specific Gravity
Cu_2S	PbS	
10	90	6.748
20	80	6.266
30	70	
40	60	6.079
50	50	
60	40	5.480
70	30	5.396
80	20	
90	10	5.364

C. The binaries PbS-FeS

Composition in %		Specific Gravity
PbS	FeS	
10	90	5.106
20	80	5.287
30	70	5.342
40	60	5.434
50	50	5.718
60	40	5.801
70	30	6.182
80	20	6.640
90	10	6.491

D. The ternaries Cu_2S-FeS-PbS

Composition in %			Specific Gravity
Cu_2S	FeS	PbS	
10	10	80	5.858
10	20	70	5.720
10	30	60	5.840
10	40	50	5.751
10	50	40	5.385
10	60	30	5.220
10	70	20	5.052
20	10	70	
20	20	60	
20	30	50	5.577
20	40	40	5.498
20	50	30	5.332
20	60	20	4.979
20	70	10	4.656
30	10	60	5.822
30	20	50	5.790
30	30	40	5.472
30	40	30	5.246
30	50	20	5.087
30	60	10	4.950
40	10	50	5.792
40	20	40	5.604
40	30	30	5.377
40	40	20	5.079
40	50	10	4.950
50	10	40	5.805
50	20	30	5.503
50	30	20	5.355
50	40	10	4.923
60	10	30	
60	20	20	5.193
60	30	10	5.132
70	10	20	
70	20	10	4.949
80	10	10	

Conclusions

The specific gravity of the ternary mattes Cu_2S-FeS-PbS were determined and the results plotted on an equilateral triangle. Lines of equal specific gravity were sketched, and these indicated that a model would have a gentle, fairly uniform slope from the PbS corner towards the center of the Cu_2S-FeS side. Because there are lines of equal specific gravity, on which an infinite number of ternary mattes would lie, it would be impossible to use the specific gravity of a matte as an index of its composition.

The macrographic examination of the solidified mattes indicated that there was an area of immiscibility adjoining the Cu_2S-PbS side. Chemical analysis and microscopic examination did not confirm these conclusions. In as much as the temperature and the time factors were evidently adequate to allow complete mixing of the molten contents of the crucible, there remains no doubt that this field of immiscibility actually exists.

The work on and the writing of this thesis was done in collaboration with Dr. Curtis L. Wilson, Professor of Metallurgy at the Montana ~~State~~ School of Mines.