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APPLICATION OF THE COMPUTATIONAL THERMODYNAMICS TOOL IN THE SIMULATION OF PYROMETALLURGICAL OPERATIONS OF LEAD-ACID BATTERY RECYCLING

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Abstract. This work, carried out with the application of computational thermodynamics, deals with the fundamentals of lead production through the recycling of lead-acid batteries. The objective of this work was to evaluate the understanding of the thermodynamic balances of the steps that are established during the process, to contribute to the improvement of operational control and recovery of Pb, which is the main element to be recovered. The research methodology carried out at the Department of Mechanical Engineering of the Federal University of Paraná (UFPR) and the Department of Metallurgy of the Federal University of Rio Grande do Sul (UFRGS), focused on using the FactSage software version 7.0, which consists of a series of FactPS, FToxid, FTsalt and FTmisc modules, with their respective databases. To address the equilibrium steps of a system, we used the thermodynamic equilibrium module that was based on the minimization of the Gibbs Energy, which once specified, the atomic species of a system "react" until reaching a state of chemical equilibrium. The software in this case determines which phases are present in the equilibrium state and calculates the concentration of the constituents in the respective phases. The diagrams are calculated in the module 'Phase Diagram' from information and parameters entered (partial pressure and temperature) and the limits of the phases are marked automatically, and you can add tie-lines manually. Analyzing specifically the case of lead (Pb) and its recovery process from lead-acid batteries, it is possible to conclude that it presents intrinsic difficulties, because the process takes place by batch in rotary furnaces. Therefore, (i) one cannot associate a certain step of the process with a certain location of the reactor, as would be for example, the case of a continuous reactor such as the blast furnace, where chemical reactions take place at known points in the furnace, and (ii) time is also a variable. Even so, there are regions where certain steps can be located, such as the oxidation of sulfides at the top of the charge and the reduction of oxides at the bottom. Thus, the diagrams presented and discussed based on the reviews found in the literature represent and validate the pyrometallurgical process with their respective areas of predominance, especially in the ustulation stage and in the lead/matte separation step, presenting the effect of the addition of iron (Fe) to the system, reducing the Pb content in the final residue, showing the importance of simulating and analyzing the process thermodynamically and also from the environmental point of view.

Keywords: Computational thermodynamics, Thermodynamic equilibrium, Pyrometallurgical process, environment.

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1. INTRODUCTION

During pyrometallurgical operations in the lead-acid battery recycling industry, a small loss of metallic Pb to the slag occurs by reduction. However, as Pb is a highly polluting input or raw material, it is important to improve the operational control in order to obtain the highest possible yield of this metal, with the aid of thermodynamics. Undoubtedly, the knowledge of thermodynamic data regarding the equilibria that involve operations and systems are pertinent and have played a key role in this aspect (GOMES, 2019).

Computational thermodynamics is an appropriate tool to deepen the control of Pb during the pyrometallurgical process, because it is able to provide information about solutions and concentration of its constituents, in a given complex system, being it multicomponent or multiphase, considering some conditions such as temperature and pressure. It is necessary, however, to validate the results obtained, through the use of software capable of performing simulations (predictions) in different areas, with those obtained through equations and thermodynamic data from the literature, which are specific to a given system. Only in this way is it possible to validate the results of simulations involving more complex systems such as Pb-O-S and Pb-S-Fe (GOMES *et al.* 2022).

The thermodynamic simulation addresses equilibrium steps of a system that, in this case, consist of the operating conditions existing in rotary lead smelting furnaces that process the loads in batches, where the rotation provides better contact between the reactants (materials) and the heat transfer. At the end of the operation, fused slag and Pb are separated (ARNOUT *et al.* 2011; GOMES, 2019).

The simulation was performed using the FactSage software version 7.0, which consists of a series of FactPS, FToxid, FTsalt and FTmisc modules, with their respective databases. From the input of user-defined information, using the available databases that allow access and manipulation of appropriate chemical species, pure and in the form of solutions, and with the choice of different modules, it is possible to perform a variety of thermochemical calculations and generate tables, graphs or figures of interest. For the simulation of the process, the thermodynamic equilibrium modulus was used, which is based on the minimization of the Gibbs energy, which once specified, the atomic species of a system 'react' until reaching a state of chemical equilibrium (ERIKSSON *et al.*, 1990 and PETERSEN *et al.* 2007).

The software determines which phases are present in the equilibrium state, their quantities and calculates the concentration of the constituents in the solution-type phases. The user needs to go through three steps:

I. define the atomic (or chemical) reactant species;
II. select all possible phases, compounds and solutions, candidates for thermodynamic equilibrium;
III. determine the final conditions (T, P or others).

The equilibrium conditions must satisfy the mass balance with respect to the components of the system and correspond to the lowest possible Gibbs energy in the selection of possible 'products'

The diagrams presented and discussed based on the reviews found in the literature represent and validate the pyrometallurgical process with their respective areas of predominance, presenting the effect of the addition of iron (Fe) to the system, reducing the Pb content in the final residue, as well as the steps, roasting, reduction, lead/matte separation and slag formation, showing the importance of simulating and analyzing the process thermodynamically and also from the environmental point of view (GOMES, 2019; GOMES *et al.*, 2022).

2. MATERIALS AND METHODS

2.1 Thermodynamic modeling

In the attempt to model a process or some stages of a process, we have the premise that a global thermodynamic equilibrium is established between the phases, and in the same way, the result of this global determination will provide us with a prediction and an alternative idea of a real situation of the local equilibria for the understanding of the process as a whole. It was then chosen to work in this research the stages of ustulation and the lead/matte separation, restricting to the effect of Fe in the system (ERIKSSON *et al.*, 1990 and PETERSEN *et al.*, 2007).

In the case of thermodynamics, the simulation has no prediction of the behavior of the system over time, being necessary for this the knowledge of the kinetics of the different stages. Kinetics, however, is not reduced to chemical kinetics, but must also include the limitations corresponding to heat and mass transfer. It is concluded that this model, because it is technically complex, and is valid only for one type of reactor, in this case the rotary one, presents relevant data for the simulation of the steps. Currently, applications of FactSage include hydrometallurgy and electrometallurgy processes, presenting calculations and tracing binary, ternary and multicomponent phase diagrams with a wide variety of axes (ARNOUT *et al.*, 2011 and BALE *et al.*, 2016).

The FactSage 7.0 main menu (Figure 1) provides access to the various modules in the package. The modules are grouped into four categories: 1. Information, 2. Databases, 3. Calculate and 4. Manipulate (results) (FACTSAGE, 2023).
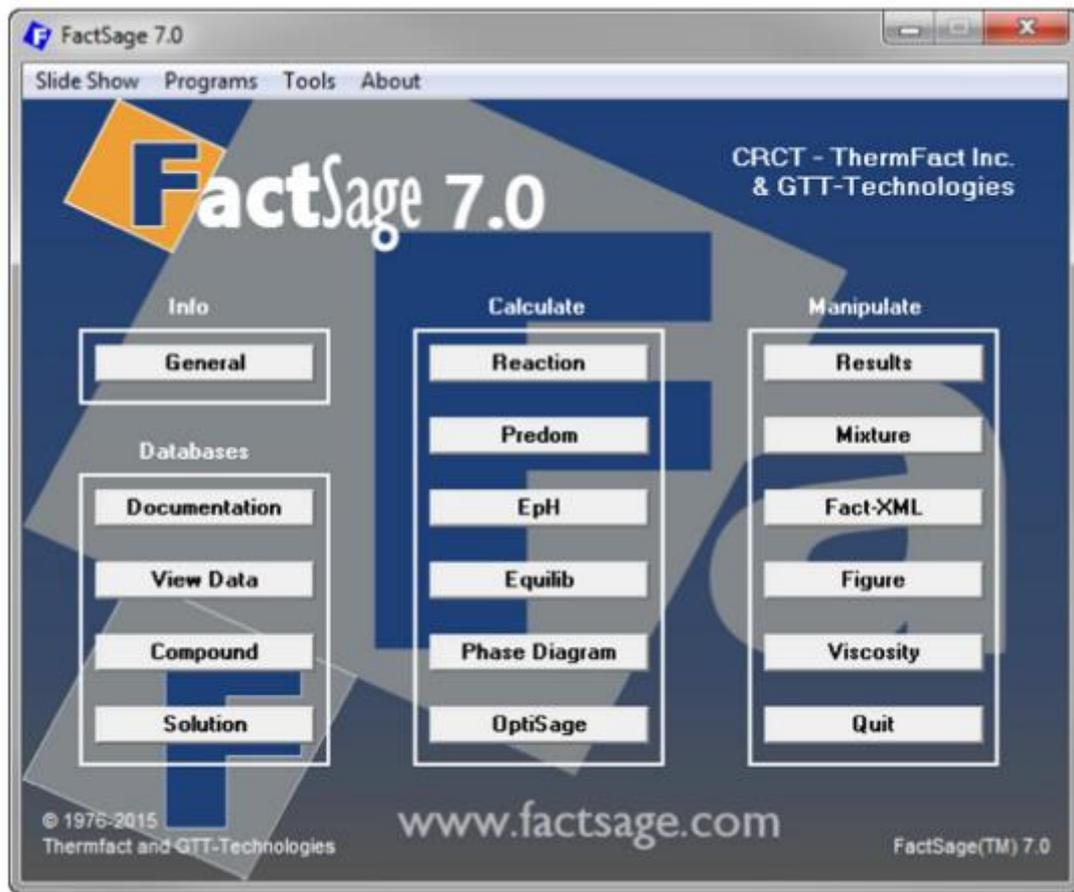
Figure 1. FactSage 7.0 - Start menu (FACTSAGE, 2023).

2.2 Information and database

FactSage provides access to solution and compound databases, where you have model parameters optimized for the Gibbs energy of the solution phases as a function of composition, pressure, and temperature.

2.3 Mdata annipulation and calculation of phase diagrams

The software offers a variety of ways to interact with the modules during the calculations (macro processing), and after the calculations through the post-processing of the tabular and graphical results of the complex equilibrium calculations in Equilib and Phase Diagram (flows, results module, Fact-XML) (BALE *et al.* 2002 and BALE *et al.* 2008). In the Phase Diagram module, two thermodynamic properties are plotted on the X and Y axes, while the other properties are held constant. The properties that can be selected as axes or constants are::

- T (ºC) – temperature;
- P – total pressure;
- V – volume;
- Comp – Composition (molar fractions, molar ratios, fractions by weight, ratios by weight);
- Potl – Chemical potentials (RT ln (ai), RT ln (Pi), log (ai), log (Pi) where ai and Pi = activity or partial pressure of component i);
- Delta H – Enthalpy relative to a standard state temperature.

In addition, various projections (e.g., liquidus surfaces) can be calculated. A unique and very useful feature of FactSage allows the calculation of the quantities and compositions of all phases in equilibrium at any point on the diagram. The diagrams are calculated in the module 'Phase Diagram' and the limits of the phases are marked automatically (one can add tie-lines manually – a feature widely used in this dissertation). In some cases, the text can be edited and adding symbols using the editing features of the 'Figure' module is also possible. Dealing now specifically with the case of lead and its recycling process from lead-acid batteries, it can be said that it presents intrinsic difficulties, because the process takes place by batch and in a rotary kiln (BALE *et al.,* 2013 and BALE *et al.,* 2016).

Therefore, (i) one cannot associate a certain step of the process with a certain location of the reactor (as would be the case of a continuous reactor such as the blast furnace, where chemical reactions take place at known points in the furnace), and (ii) time is also a variable (GOMES, 2019).

Even so, roughly speaking, there are regions where certain steps can be located – such as, for example, the oxidation of sulfides occurs at the top of the charge and the reduction of oxides at the bottom (BALE *et al.,* 2016). Thus, the figures of the dissertation properly represent the chemical processes, maintaining a certain independence from the regions where they occur. Remembering, the furnace charge consists basically of metallic lead, oxides and lead sulfate. A solid reducer (anthracitic coal or petroleum coke) and metallic iron (steel scrap, typically in the form of chips) are added to the raw material. Sodium is added in the form of sodium carbonate for chemical reasons (to minimize the generation of SO_2) and cost.

3. RESULTS AND DISCUSSION

3.1 Roasting step

This process can be followed by means of a simplified Kellogg diagram (predominance area diagram), Figure 2. It is observed that, starting from the lead sulfate contained in the batteries, one must obtain a state of thermodynamic equilibrium such that both the partial pressure of oxygen and the partial pressure of SO_2 in equilibrium are low to reach the area where the liquid lead is stable. Lead sulfate, depending on the condition of the atmosphere, can turn into oxide (ustulation). The oxide formed from the sulfate can be reduced to liquid lead along with the charge material that entered the process under this chemical (oxidized) form (GOMES, 2019 and GOMES et al., 2022).
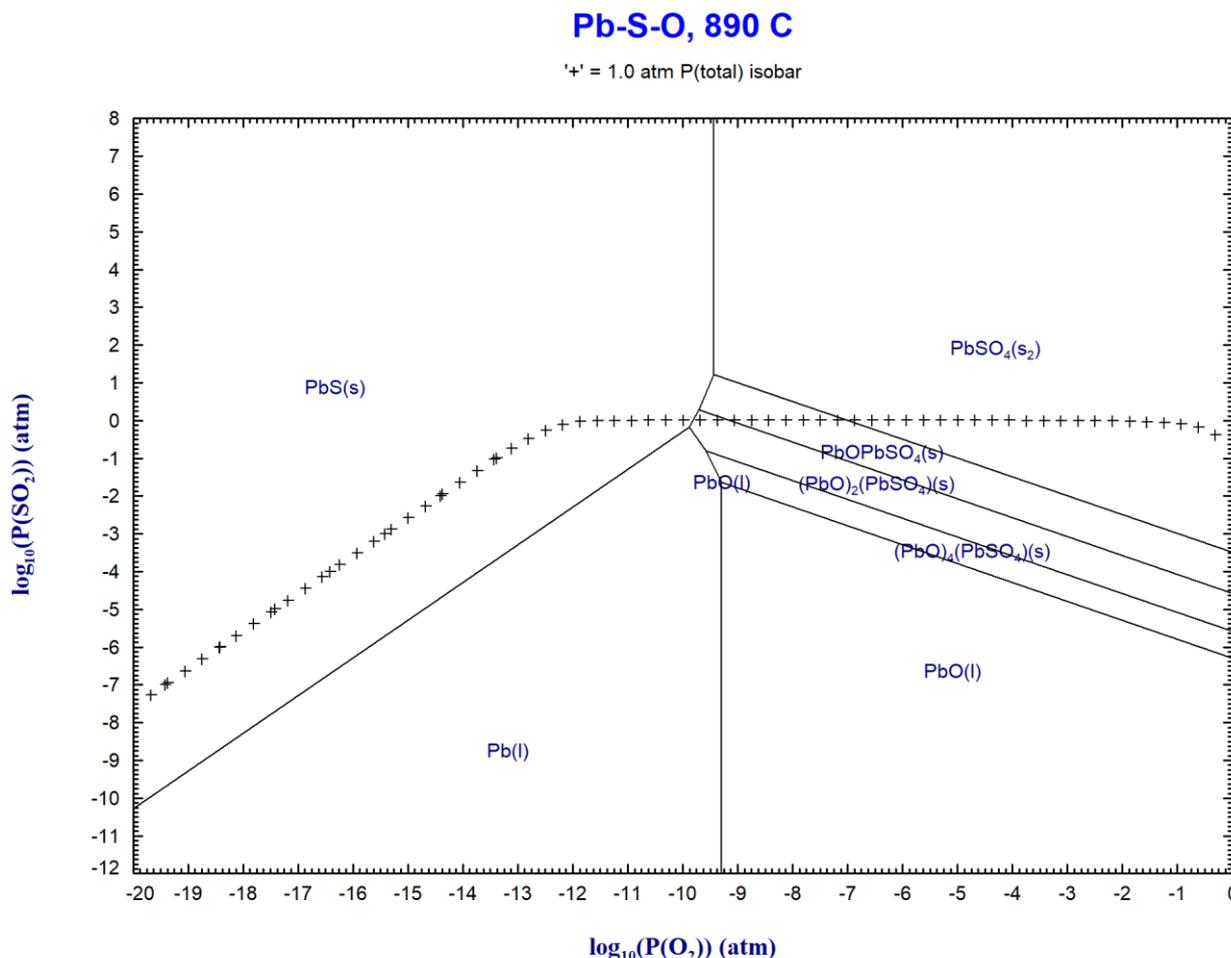

Figure 2. Diagram of areas of predominance (Kellogg diagram) for lead (schematic), 890°C. Source: GOMES, 2019 and GOMES *et al.* 2022

Now, already working with FactSage, the first of the graphs produced shows the situation of the diagram of areas of predominance (Kellogg diagram), cited above, for the temperature of 890°C. It roughly corresponds to the figure shown

in the generic diagram. The same logic is found here, where it can be seen that the sulfate coming from the scrap of the battery, when gradually losing the sulfur (by the supply of oxygen, that is, by ustulation), gradually becomes an oxide. The process can be tracked in the diagram as a compound $(PbO)x(PbSO_4)$, in which the ratio of PbO to $PbSO_4$ increases significantly toward PbO. It can also be seen that it is possible to reduce PbO to lead by eliminating oxygen (oxide reduction process). Ustulation occurs in an atmosphere that theoretically contains the gases O_2, SO_2, SO_3 and S_2. The follow-up of the process, in the case of Figure 3, was done in a traditional way, using the partial pressures of SO_2 and O_2.
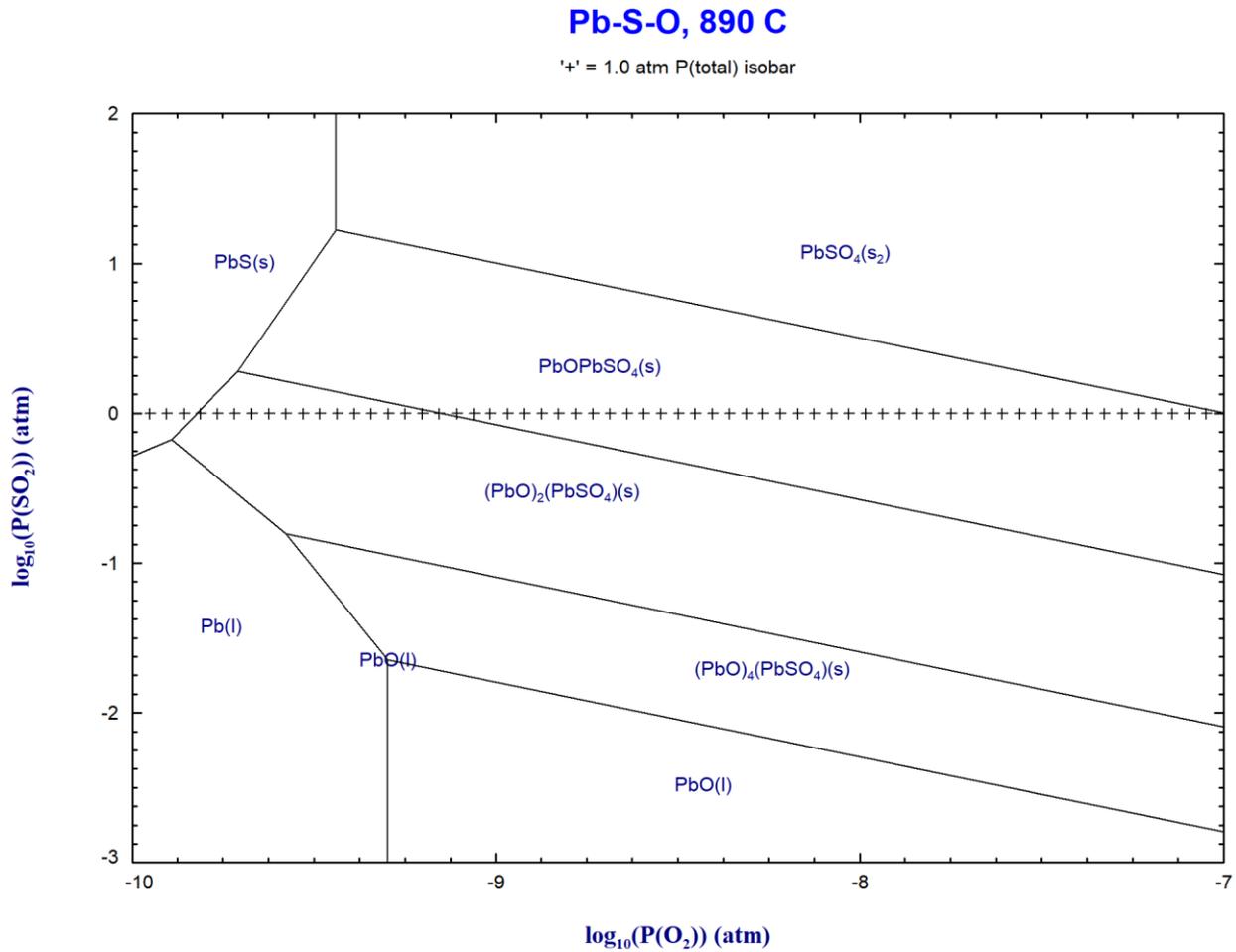

Figure 3. Diagram of areas of predominance, Pb-O-S system, as a function of the partial pressures of SO_2 and O_2, 890°C. Source: GOMES, 2019.

3.2 Lead/matte separation step

In this lead/matte separation step, we address the main objective of the work which is about the effect of Fe on the system. The discussion begins with the elimination of sulfur contained in the metal (liquid lead) due to the existence of a 'miscibility gap' in the ternary diagram Pb-S-Fe that will be presented below. The existence of this gap becomes timely, because without it the extractive metallurgy of secondary lead would have to seek another form of elimination of S. In the case of the simulation, to analyze the miscibility gap was traced the isothermal diagram of phases (cut in the Fe-Pb-S system) at a temperature of 1200°C, Figure 4 (GOMES, 2019; GOMES *et al.*, 2023).
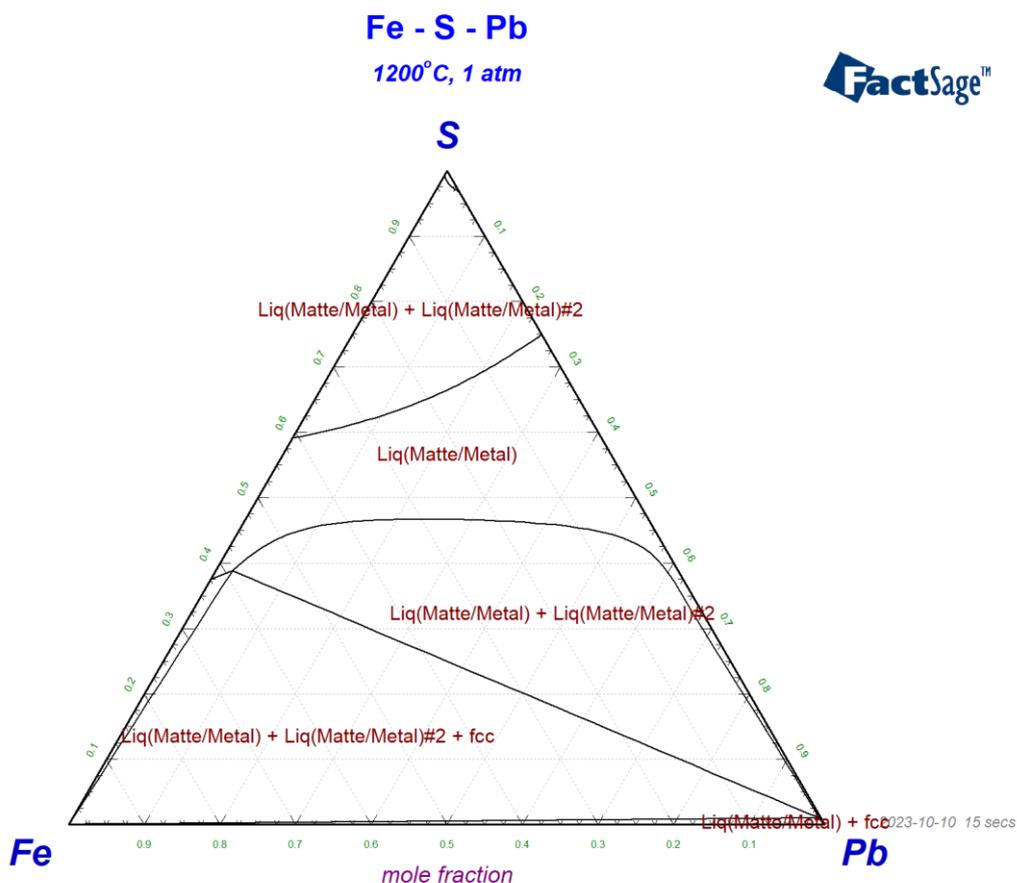
Figure 4. Phase diagram Pb − S − Fe, corner rich in Pb, 1200ºC; Tie-lines, connect the "two" liquid phases in equilibrium (liquid lead and matte). Source: GOMES, 2019.

From this diagram it can be seen that the addition of a little iron (from scrap) to the Pb-S system produces a liquid triple alloy Pb-S-Fe, however, if more iron is added to the system it causes a separation of the original liquid phase into two others, that is: one of the liquids is constituted in the 'lead' (in fact it is a solution very rich in lead) with low contents of S and Fe,   which impurify him, while the other collects these elements, and is called matte. Despite the names, it is thermodynamically the same liquid phase, but with different compositions. The dashed lines that connect the compositions of the two liquids in equilibrium (connecting lines, or tie-lines) are very important in this case. Due to its relevance, this situation was recalculated for the 'corner of the Pb', at the same temperature of 1200°C, Figure 5 (GOMES, 2019).
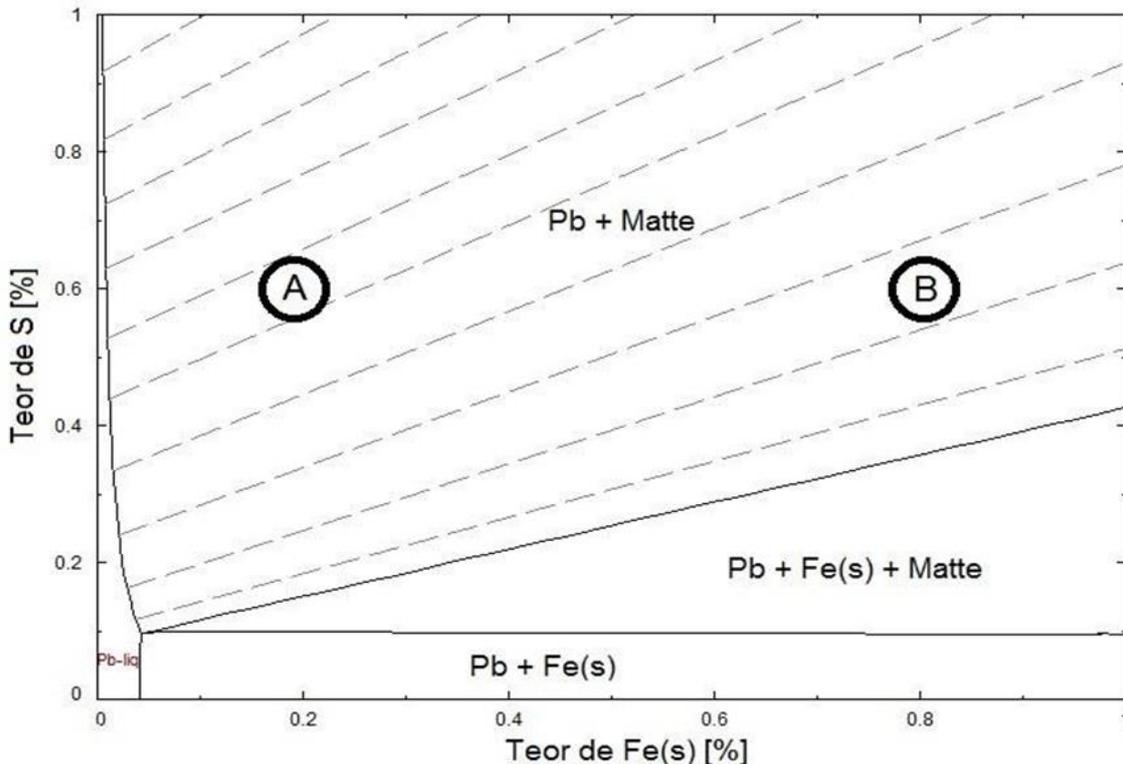
Figure 5. Phase diagram Pb-S-Fe, corner of Pb, 1200 °C, showing the tie-lines connecting the two liquids in equilibrium (liquid lead and matte) for different compositions; for explanations of points A and B see text. Source: (GOMES, 2019).

The results of these two simulations can be seen in Table 1.

Table 1. Compositions of phases in equilibrium: liquid and matte lead, Pb-S-Fe system. Source: (GOMES, 2019).

Cases	Phase	Fe [%]	S [%]	Pb [%]
Case A	Liquid lead	0,01	0,5	99,5
	Matte/Slag	31,0	21,0	48,1
Case B	Liquid lead	0,02	0,2	99,8
	Matte/Slag	45,0	24,0	31,4

It is verified with the simulation the beneficial effect of Fe in the system. According to the results, the presence of this metal has the ability to lower the S content present in the crude lead, from 0.6% (without Fe) to 0.5% (with 0.2% Fe in the system, point A). By increasing the iron content from 0.2% to 0.8% Fe (point B), the sulphur content falls from 0.5% to 0.2% (a decrease of more than half in the initial S content). The content of dissolved Fe in liquid lead, on the other hand, increases by 100%, from 0.01% to 0.02%, however, the absolute values of this element dissolved in liquid Pb are minimal, making this fact less worrisome. In the process, the matte will be discarded (see stage of the formation of the slag). In case A of Figure 5, although the Pb content in the matte is high, approximately 50% (large waste of Pb), the proportion of this liquid to the liquid Pb (as can be verified by the composition of the point), is small (that is, the lever rule, applied in the specific tie-line, shows that the matte mass is small,   or contemptible). For point B increases a little the proportion of matte, in compensation, the content of Pb 'lost' decreases to approximately 30%. The lowest S content is obtained with the saturation of the bath in Fe. In this case the system is in the three-phase field containing solid Fe, matte and liquid lead.

4. FINAL CONSIDERATIONS

The Pb, throughout the process, ends up accompanying the slag (in the transformation of the matte into slag) giving it the character of hazardous waste. Now this aspect, the fundamental issue – which is the dissolution of the oxygen necessary for the transformation – is fully contemplated and has been presented at the respective stage. Returning to the lead that would be contained in the matte, it can be said that, with the oxidation of the matte inside and with the subsequent cooling outside the furnace, it is presumed to assume that part of this element passes to the chemical form of oxide. It is also possible that it can still be found in the slag in metallic form – by the stability ensured by the high nobility of the

metal (already pointed out earlier). In this case, its presence in the slag would be due to merely mechanical issues: it can become ingrained in the slag, or in the matte that gave rise to it, by the question of the movement of the rotary kiln.

An interesting fact is the possibility of using one of the 'slag' phases (FToxid-SlagA) of the FToxid database to represent the matte with a low degree of oxidation; This is possible given that its modeling admits a good amount of sulfur – in addition to lead, iron, oxygen, and also sodium. The importance of this will be seen below. The important role that sodium plays in the elimination of sulfur was left out in the early part of this work because of the limitations imposed by ternary systems; On the basis of the provisions just presented, however, this role can be examined below. As has been seen, during the lead oxide reduction step, the sulfur ends up dissolving in the liquid metal (both the newly formed and the one resulting from the fusion of the metal already present in the scrap) impurifying it. The presence of Fe causes, as also already seen, the separation of the liquid bath into matte and raw lead. Most sulfur tends to concentrate in matte, leaving a non-negligible S content in liquid lead. Using the FToxid-SlagA phase to represent the matte with more complex composition it is possible to verify the influence of Na in the process.

The thermodynamic simulation made to analyze this case shows that, starting from an established amount of substances representative of the load of a rotary kiln (500 kg Pb, 150 kg PbO_2, 350 kg $PbSO_4$, 50 kg Fe and 60 kg of C) – still without the presence of sodium – at a temperature of 950 °C, they remain in the liquid Pb, after the simulation of the reactions, approximately 6 % of the S present in the system (which gives a content of 0,3 % S in the liquid Pb).

The role of sodium becomes clear when the results after adding (50 kg) Na_2CO_3 to the system are analyzed. It is verified, through the simulation, that, among other positive factors, the sulfur content in lead falls to a value of only 0.04 % (Table 2). It is therefore possible to verify, by the simulation, the expected (positive) effect of the elimination of sulphur in raw lead by sodium.

Table 2. Action of sodium in the recycling of lead from batteries in view of the distribution of S in the different phases: matte, Pb and atmosphere and its content in matte and Pb (GOMES, 2019).

Sulphur	Phase	Without Na	With Na
Distribution sulphur in the system [%]	Gas	1,3	0,2
	Matte/Slag	92,2	99,0
	Lead	6,5	0,8
Sulphur content [%]	Liquid Pb	0,3	0,04
	Matte/Slag	27,0	30,5

Another interesting factor is to find that the fraction of S contained in the gas phase is reduced, from 1.3 to 0.2 % – which means that the sulfur originally present in $FeSO_4$ was transferred to the matte and not to the atmosphere of the furnace.

5. CONCLUSIONS

Analyzing the present work, it can be concluded that:

The fundamental questions of the thermodynamic simulation of the secondary lead production process by the recycling of lead-acid batteries proposed in this analysis – in parallel in the literature, were met.

The use of the stages of roasting and lead/matte separation made it possible to simulate each of them taking into account their conditions and particularities such as the role of iron endo beneficial to the system.

6. ACKNOWLEDGMENTS

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