

Synthesis and Thermal decomposition of Lead Citrate

Srecko Stopic, Thomas Träger and Bernd Friedrich

IME Process Metallurgy and Metal Recycling, RWTH Aachen University.
Intzestrasse 3, 52 056 Aachen, Germany

Abstract

In this study, as part of developing a new process which can avoid smelting and electro-winning, citric acid was used for dissolution of waste lead paste in order to produce lead citrate. Leaching experiments were performed in laboratory conditions in 1 l. Scale up was performed and in 200 L reactor. The thermal decomposition of prepared lead citrate was performed in neutral and oxidizing atmosphere between 280°C and 340°C in 60 min. DTA and TGA analysis were shown that dehydration was virtually complete before thermal decomposition. Optimal thermal decomposition conditions were determined by investigating the effect of flow rate and type of protective atmosphere. Different solid products were produced depending on reaction

1 Introduction

Lead-acid batteries are widely used for storage in backup power supplies in cell phone towers, high-availability settings like hospitals, and stand-alone power systems. In most of the applications where lead is used, especially lead-based batteries, it is possible to recover metals for use over and over again without any loss in quality [1]. Furthermore, as all lead-based batteries have the same basic chemistry, this means that all types of lead battery can be processed easily by lead smelters. Nowadays, there has been a continuing interest in improving the electrode active material quality in lead-acid storage batteries to increase energy efficiency and decrease of operational costs for recycling. Mahato and Laird [2] have studied various additives, commonly referred to as expanders, which have been used particularly in the paste for making negative battery plates. It is known that expanders improve the efficiency of utilization of the active materials, particularly, the high rate, low temperature discharge capacity and the operational life of the battery. But, in last time the recycling of lead paste from lead acid batteries is main focus of different studies. Two ISASMELT™ plants [2] have been constructed to date for recycling lead batteries, producing fine lead and a low-lead silicate slag. Smelting and using iron (Fe) to ‘fix’ the sulphur component also generates a haz-



ardous FeS-PbS matte. Furthermore, alternative processes using short-rotary furnaces, hydrometallurgy and electro-winning have their own share of toxic by-products, and are capital and energy intensive.

Kumar [3] has developed new strategies for recycling of lead-acid batteries and patented such that precursors for battery plates are directly produced in an environmentally sound process that is sustainable with respect to both materials and energy. The method reduces energy consumption as well as carbon and sulphur dioxide emissions, compared to existing approaches. His team has extracted lead from spent batteries used in vehicles, back-up telecommunication facilities and power generating stations by reacting active lead sulphate (PbSO_4) paste in a non-hazardous aqueous solution [4]. The chemicals used are organic reagents such as carboxylic acid and salts. The paste is decomposed to produce a sodium sulphate by-product, while lead is crystallized into an organic precursor. Once subjected to combustion-calcination at 350°C , lead oxide (PbO) granules are generated for reuse in battery manufacture. Kumar added that an availability of a sustainable technology will increase incentives for advanced lead batteries that can deliver much higher energy and power densities for electrical vehicle applications. Zhu et al. [7] prepared the lead citrate precursor, $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$, by leaching desulfurized paste with citric acid and H_2O_2 . Ultra-fine PbO/Pb powder with particle size of 100–500 nm was obtained at 370°C after thermal decomposition of lead citrate.

The aim of this study was synthesis of lead citrate from waste lead paste and especially to test scale up in order to produce 10 kg of lead citrate. Thermal decomposition of prepared lead citrate was investigated in different protective atmospheres in order to prevent the formation of undesired lead.

2 Experimental work

2.1 Material

The obtained paste scrap was shown at Figure 1. Moisture contents amounts between 6 and 7 wt % in a tested paste scrap. Free lead content determined by wet chemistry is about 32 wt %. Chemical composition of lead compounds was determined using XRD-analysis and presented in Table 1:



Figure 1: Paste Scrap

XRD-Analysis was performed using a sieved lead bearing components. Limitation of XRD-analysis is that this method sees crystalline material (non-amorphous material). The accuracy of method amounts about 4 wt %.

Table 1: The presence of lead compounds in Paste Scrap

Lead compounds	Mean composition (Wt. % in dry sample)
Pb	32
α -PbO	1.2
4 PbO·PbSO ₄	3.0
PbO·PbSO ₄ ·H ₂ O	13
PbSO ₄	27.8
2 PbCO ₃ ·Pb(OH) ₂	2.0
α -PbO ₂	7.5
β -PbO ₂	12

2.1 Leaching

2.1.1. Leaching in Laboratory conditions

The paste scrap was firstly dried at 70°C over the night and dissolved in a 1 L scale under an atmospheric (glass beaker) using citric acid, acetic acid and small additives of sodium hydroxide and hydrogen oxide.. Temperature was controlled within ± 3 °C by a temperature control system,



manipulating both a water cooling system (see Figure 1). Agitation was provided by an impeller that is motor driven. A certain amount of lead paste was mixed with a pre-calculated amount of deionised water. Then the slurry was heated up to a predetermined temperature under continuous agitation. Upon temperature stabilisation, first sampling was performed. Precipitation follows the leaching process.



Figure 2: Leaching of a dried lead scrap in laboratory conditions

2.1.2. Scale up of leaching

After first investigation of optimal parameters in laboratory conditions in volume of 1 l a similar procedure was investigated in 200 L reactor, as shown at Fig. 3.



Figure 3: Leaching in 200-L reactor

After drying and sieving the fraction under 500 μm was dissolved using appropriate quantities of citric acid, acetic acid, sodium hydroxide and hydrogen peroxide. The leaching experiments were performed at 60°C in 6 hours with an injection of protective gas over the night. After filtration and drying the obtained lead citrate (as shown in Fig. 4) was analyzed and decomposed.



Figure 4: Produced lead citrate

2.1.3. Thermal decomposition of lead citrate

Decomposition of lead citrate was performed in non-isothermal and isothermal conditions. DTA and TGA analysis was shown at Figure 5.

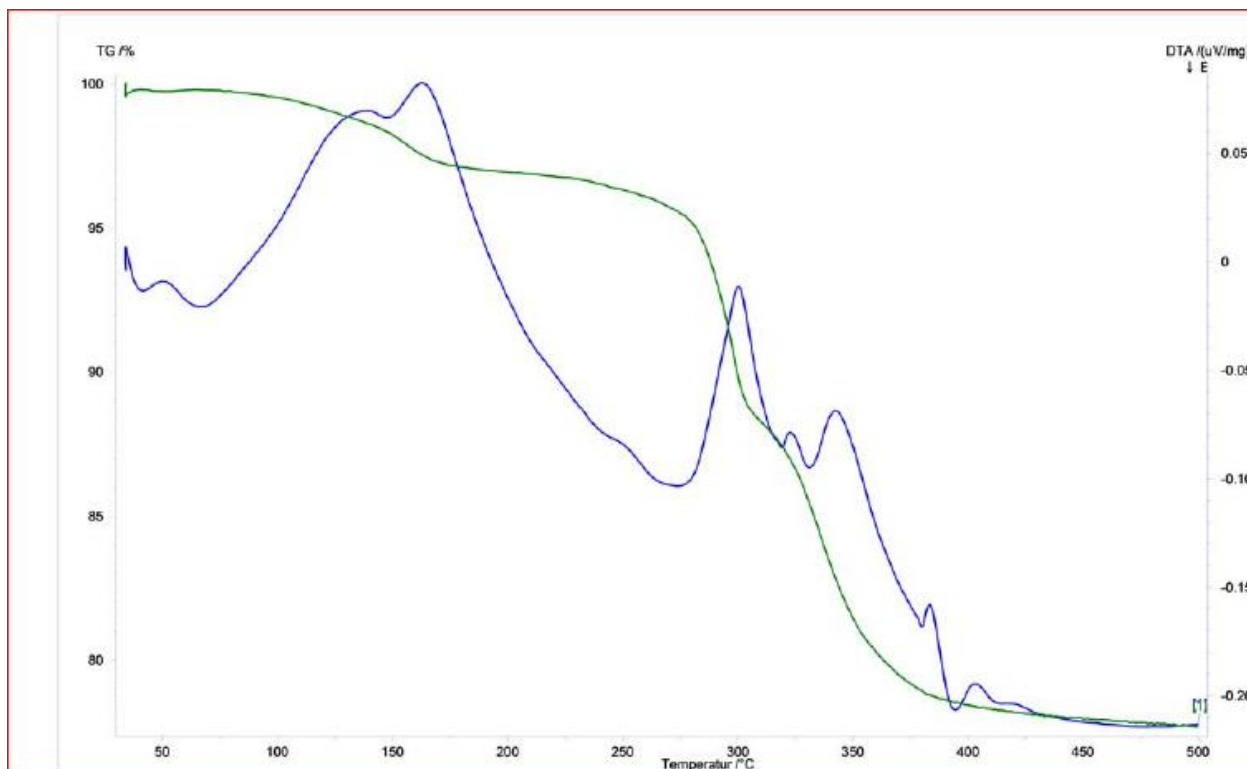
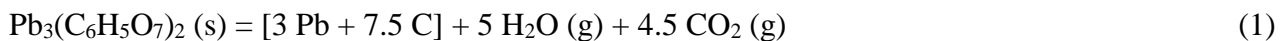


Figure 5: DTA/TGA analysis of thermal decomposition of lead citrate in argon



As shown at Figure 5 the thermal decomposition of lead citrate in inert atmosphere takes place in two main stages: dehydration of water and formation of metallic phases and gaseous phase. Generally, the thermal decomposition of metal carboxylates in oxidizing atmospheres leads to formation of the metal oxides, carbon dioxide and water. In inert atmospheres, however, the solid products may be the metal and /or the metal carbide and possible some carbon. For lead carboxylates, the formation of metal rather than PbO is thermodynamically favored, although a mixture of PbO and Pb is reported as the product of the thermal decomposition of lead oxalate. Brown [5] proposed the stoichiometry of the decomposition of lead citrate, after initial dehydration steps:



Therefore an influence of different protective atmospheres in order to control the final solid products was studied (as shown in Table 2). The experiments were performed below the melting point of lead in order to prevent formation of molten lead, which is undesired product for this thermal decomposition.

Table 2: Decomposition of lead citrate (heating rate 25 K/min, residence time 60 min)

Gas	N ₂	Air	Air/H ₂ O	N ₂ /Air	N ₂ /Air
Flow rate (l/min)	3	3	3/4	1.5/1.5	1.5/1.5
Temperature (°C)	310	310	310	310	280

During this process the next phases were formed: main phase β -PbO; and intermediate phase: α -PbO, metallic Pb and Lead oxide hydrate (only present in nitrogen atmosphere)

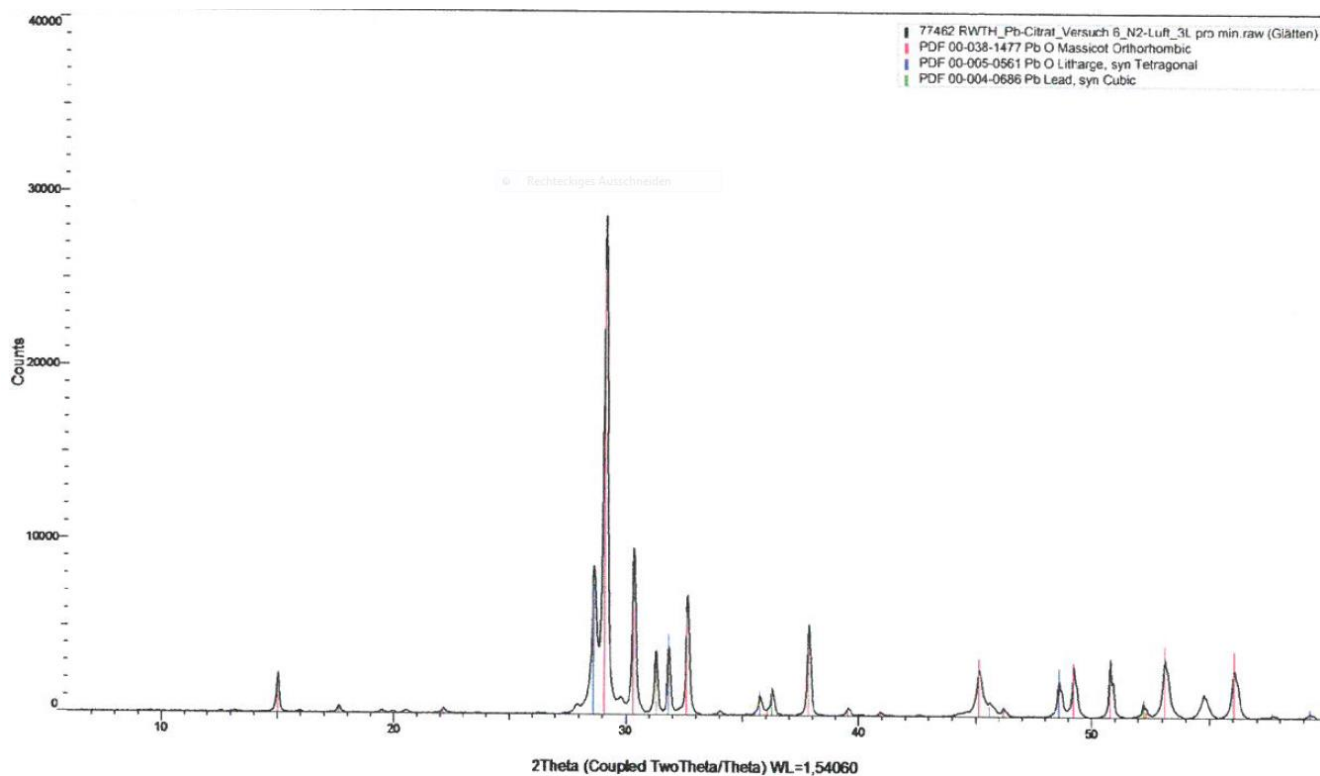


Figure 6. Typical XRD-analysis in nitrogen and air atmosphere

3. Conclusion

In this study, a new process for the synthesis of lead citrate from paste scrap using citric acid was successfully applied. Leaching experiments were performed in laboratory conditions in 1 L reactor. Then using same procedure scale up was performed in 200 L reactor. The thermal decomposition of prepared lead citrate was investigated in non-isothermal conditions (DTA and TGA analysis) and then in a rotary furnace in isothermal conditions in order to test different protective atmospheres. During this process the next phases were formed: main phase: β -PbO; and intermediate phase: α -PbO, metallic Pb and Lead oxide hydrate (only present in nitrogen Atmosphere)

4 References

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