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BENEFICIATION OF PVC WASTES IN IRON OXIDE REDUCTION

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Abstract

This study aims at using wastes of Polyvinyl Chloride (PVC) as alternative reducing agents in iron metallurgy. Thermal behaviors, in air atmosphere, of PVC waste and pure PVC were studied between 225 and 900 °C. Mixtures of hematite with both the PVC samples, were isothermally treated between 300 and 1050 °C for different durations. Solid reaction products were subjected to scanning electron microscopy, X-ray diffraction and infrared spectroscopy. The direct reduction of hematite into metallic iron, at 1000-1050 °C, by PVC hydrocarbon was proved. The reduction steps, the possible reaction mechanisms and the impact of formulation additives were also discussed.

Keywords: PVC, thermal treatment, hematite, reduction.

1. INTRODUCTION

Though the natural plastics have an ancient origin, their industrial synthesis and production became significant during the XXth century. Figures regarding to the world and European plastics production were well documented in Reference [1]. According to these data (Figure 1), about 1.5 million tons of plastics were produced worldwide in 1950 and since then their production increased significantly reaching roughly 230 million tons in 2009. A similar evolution of the plastics manufacture is valid for the European countries, which produce around 24 % of the world total. The main end-use of plastics is packaging sectors followed by building & construction, automotive and electric & electronic ones. As mentioned early [1], there are five high-volume plastics families, *i.e.* polyethylene (including PE-LD, PE-LLD, PE-HD); polypropylene (PP); polyvinyl chloride (PVC); polystyrene (PS) and polyethylene terephthalate (PET). The polyvinyl chloride is the third of the most used plastic resins. Often, additives are incorporated in the plastics, to improve their properties and performance for a specific end-use such as the so called “reinforcement” [2].

Use of plastics, as well as light metals, in the automotive industry continues to grow, leading to the decrease of the vehicle weight within limit of comfort and safety features. It is believed that a 100 kg weight reduction of a vehicle results in a fuel savings of about 0.7 L/100 km. The weight of polymers in a common car accounts for about 10 % incorporated and divided into more than one thousand cars' parts. Polypropylene, polyurethane and PVC are the plastics the most used in the vehicles. End-of-life vehicles (ELV), after dismantling are directed to shredding process. The obtained materials undergo a series of mechanical and physical separations in order to recover the ferrous and non-ferrous metals. The residue of the shredding process, called automobile shredder residue (ASR) or “car fluff”, represents about 20-25% of the ELV. A general composition of the car fluff [3] is given in Figure 2. Most of the ELV plastics, including PVC, are concentrated in the car fluff. Note that the shredder companies use, besides ELV, other materials (e.g. plastics from discarded electric and electronic assemblies) in the shredding process leading to an heterogeneous fluff depending on the input materials.

Waste disposal of the car fluff is no longer allowable and according to the directive of European Parliament and of the Council of September 18th 2000 [4], only 5 % of car fluff should be put into landfills. In this context, a project named “REFORBA” and supported by the French National Research Agency (FNRA) aimed at the thermal beneficiation of car fluff in iron metallurgy. As could be expected, the residual PVC is the most problematic case due to its chlorine and additive content. Thereby, this study is focused on the direct reduction of hematite by the hydrocarbon content of the PVC. A two steps process was envisaged. It consists in the dechlorination of the PVC at about 300 °C followed by the reduction of hematite around 1000 °C.

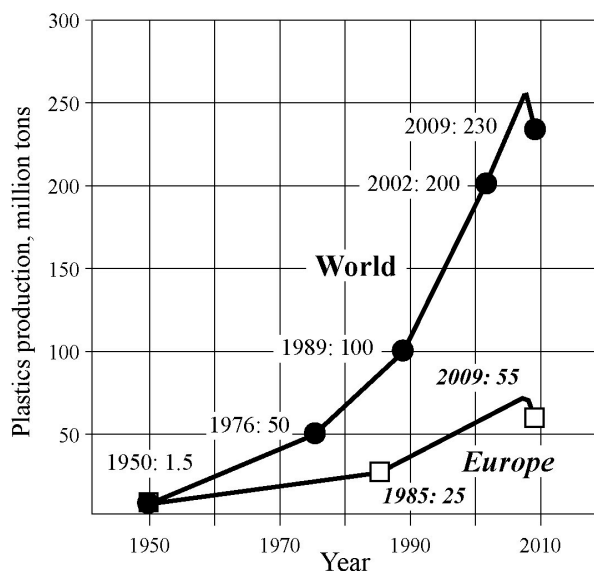


Figure 1 - Plastics production at 1950-2009.

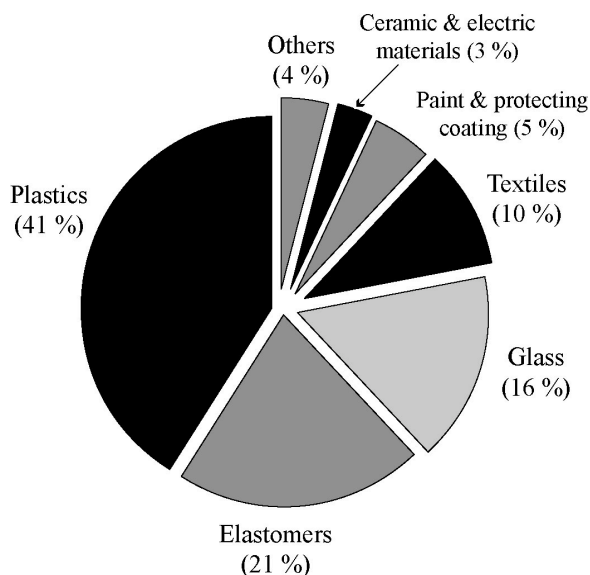


Figure 2 - Average composition of car fluff.

2. EXPERIMENTAL

Two PVC samples were used for this investigation. The first sample is wasted PVC and it is noted as PVC-1. The second sample is pure chemical grade PVC and is called PVC-2. Iron oxide, subjected to reduction, is hematite (Fe_2O_3) of high purity. All used samples were in powder state. Mixtures of PVC with hematite were conditioned as pellets by using kaolin clay as useful bonding and plasticizing agent. Obtained pellets were dried in an oven at 70 °C in order to evaporate the free water before thermal treatment and different analysis tests. The thermal behaviors of the individual samples and their mixtures were checked in horizontal experimental set-up including a static electrical furnace. Most of the tests were performed under air atmosphere for the treatment of the PVC alone. The thermal reduction of hematite containing mixtures was performed without gas circulation and/or under a low flow rate of air. Raw samples and solid reaction products were examined by scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), X-ray diffraction (XRD) and infrared (DRIFTS) spectroscopy.

3. RESULTS AND DISCUSSION

Results from the SEM-EDS analysis of the initial PVC samples are given in Figure 3. Besides chlorine and carbon, the wasted PVC sample contains other elements such as Si, Al, Ca, O and Pb (Fig. 3a). This elemental composition is in good agreement with the sample origin. It is obtained from the electric cable sheath. Calcium and lead compounds are known as heat stabilizers for the based PVC materials. As could be expected, the PVC-2 is only composed of C and Cl (Fig. 3b) which form, with hydrogen, the structure of the polyvinyl chloride. XRD results of the PVC-1 revealed the presence of calcite (CaCO_3) as main crystallized phase of the inorganic matter. Note that usually, the crystallization degree of PVC is very low.

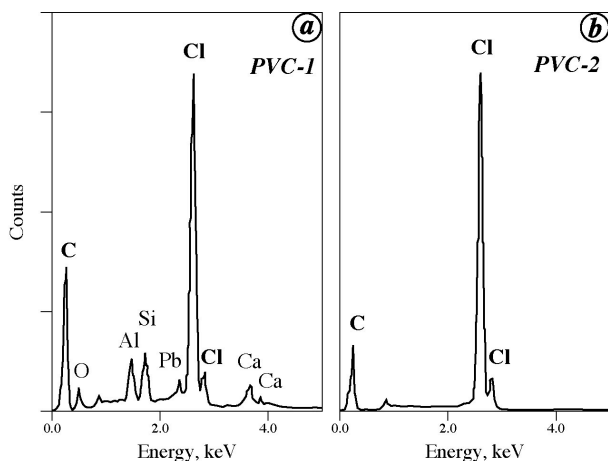


Fig. 3 - SEM-EDS spectra of the initial PVC samples.

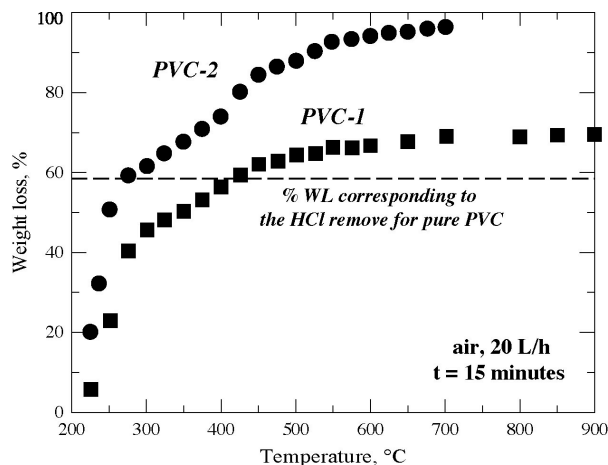


Fig. 4 - Thermal treatment of the PVC samples at different temperatures.

3.1 Behavior of the PVC samples in air atmosphere

Two series of experimental tests were carried out to follow the behavior of both the PVC samples in air atmosphere between 225 and 900 °C. Results are shown in Fig. 4 as the evolution of the percent weight loss (%WL) of the samples as a function of the temperature for a reaction time of 15 minutes. A rough examination of the % WL curves suggests that at least two phenomena should be distinguished at temperatures lower and higher than 300 °C. The first phenomenon could be attributed to a complete or partial removal of chlorine. The % WL observed at temperatures higher than 300 °C may indicate the reaction of the hydrocarbons with oxygen giving carbon oxides and water vapor as final reaction product. As shown by Fig. 5 (a), the product of PVC-1 treated at 300 °C still contains chlorine. Whilst, that of PVC-2 is almost free of chlorine. These results point out that the dechlorination of PVC depends on its additive contents.

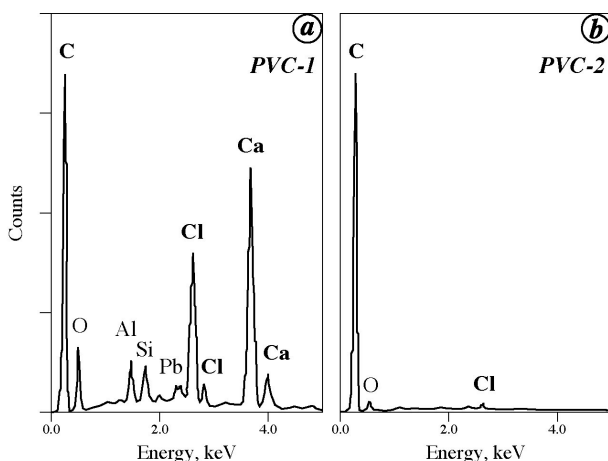


Fig. 5 - SEM-EDS spectra of the PVC samples treated at 300 °C in air.

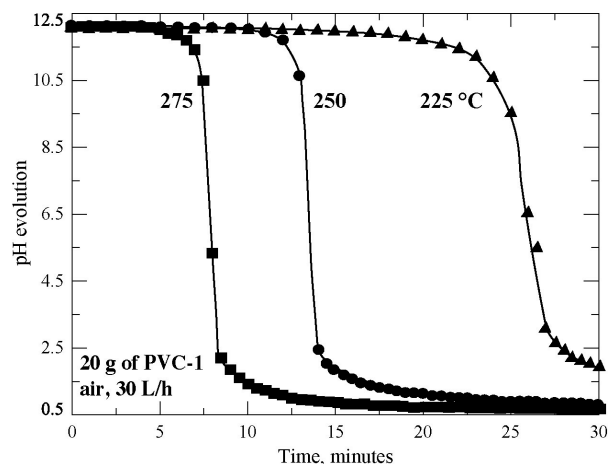


Fig. 6 - Evolution of the solution pH during trapping the outlet gas of the PVC treatment.

To have an idea about the removal kinetics of HCl from the wasted PVC sample, three thermal treatment tests of 20 grams of PVC-1 in air atmosphere were performed at 225, 250 and 275 °C. The outlet gas was immersed in a solution of 0.4 L with an initial pH equal to 12.0. The evolutions of the pH solution as a function of the reaction time are plotted in Figure 6. After a latent period, the solution pH decreased sharply reaching values around 0.5 when the treatment temperature is higher than 225 °C. Further, residence time less than or equal to 30 minutes are sufficient to ensure the removal of the “free-HCl” from the PVC. The remaining chlorine is probably associated to calcium and lead components of the PVC-1.

3.2 Direct reduction of hematite by PVC

Pellet mixtures containing (35% PVC-1 + 35% hematite + 30% clay) and (50% PVC-1 + 50% hematite) were tested in view of iron oxide reduction. Results described in section 3.1 showed that a quasi-total removal of the chlorine from PVC should be done under the form of HCl near 275 °C. Hence, these mixtures were dechlorinated at 300 °C for 30 minutes. Air is used as carrier gas for preventing and/or for slowing down any reaction of HCl with hematite. Subsequently, the dechlorinated pellets were heated from 600 to 1050 °C for 30 minutes. Several tests were also carried out at 1025 °C with a residence time from 7.5 to 240 minutes. The results are as follows:

- Reduction of hematite into magnetite by hydrocarbons of PVC started from 300 °C even in presence of air atmosphere.
- Hematite and magnetite coexist in the reduced pellets for the temperature lower than or equal to 900 °C.
- Metallic iron appeared during the direct reduction at 1000 °C. Further, crystallized fayalite (Fe_2SiO_4) was synthesized by the reaction of wüstite with quartz. Complete reduction of Fe_2SiO_4 into Fe° and SiO_2 was achieved at about 1050 °C.
- Reduced pellets contract from 1000 °C due probably to particle sintering and/or to the fusion of some components of the pellets.
- Hydrated calcium chloride was identified in the reduction product of clay free pellets. For this type of mixture, the reduction efficiency seems to be lower than that when clay is added in pellets. One may speculate that calcium chloride, surrounding iron oxide particles, acts as a diffusion barrier slowing down the reduction progress.

4. CONCLUSION

This study demonstrated the possibility of the beneficiation of wasted plastics in the iron oxide reduction. As all experimental tests are performed by using PVC alone as reducing agent, any mixture of plastics with lower content in PVC, as car fluff, will give better results. A two steps-process including dechlorination at low temperature followed by thermal treatment at 1000-1050 °C seems to be adequate for the reduction of iron oxides. The presence of several inorganic additives in the plastics avoids full removal of chlorine. This handicap should be overcome by introducing reasonable proportion of PVC in the iron metallurgy units. Use of such residual materials as reduction agent and energy supply leads the process to meet the principles of sustainable development from resource conservation and environmental points of view.

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