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# Solar thermal energy use in lead acid batteries recycling industry: A preliminary assessment of the potential in Spain and Chile.

**Elisa Alonso[1,3], Alessandro Gallo[1] and Héctor Galleguillos[2,3]**

[1] University of Antofagasta. Antofagasta Center of Energetic Development. Antofagasta (Chile)

[2] University of Antofagasta. Chemical Engineering and Mineral Processes Department. Antofagasta (Chile)

[3] Solar Energy Research Center (SERC Chile). Santiago de Chile

## Abstract

Lead acid batteries recycling industry has a significant heat demand, including processes at around 500 and 1000 ºC. Due to it, this work faces a preliminary approach to the integration of CSP technology with such an industry. A general description of the recycling process is presented as well as the thermal requirements of the different stages. Smelting and refining are retained among them and they are proposed to be provided with concentrated solar energy as source of heat. Two different locations are evaluated: Murcia, in Spain and Calama, in Chile. Combining the two processes and two locations, four cases are presented. Heliostat field and central receiver dimensions are estimated for each case and the percentage of annual solar fraction is obtained according to the energy demand. A solar multiple is considered in order to include thermal storage and to provide a constant heat demand. While in Spain the proposed solar plants are able to supply 68 and 76 % of the smelting and refining respective annual demands, in Chile the solar fraction achieves 90 and 94 %.

Keywords: *Lead-acid batteries recycling, Solar process heat, Central receiver, Spain, Chile*

## 1. Introduction

Industrial sector accounts a significant fraction of the global heat demand. For instance in the European Union the total useful heat demand in industry overpasses 4000 PJ/year and covers about 28% of the total primary energy consumption for final uses (Pardo et al., 2012). According to IEA and SolarPACES this consumption can be separated into three temperatures intervals: below 100 ºC, 100-400 º C and above 400 ºC (SHC IEA and SolarPACES, 2008) and concerning European countries, 30 percent of industrial processing requires heat below 100 ºC, 27 percent of industrial heating needs can be met with heat between 100-400 ºC, and 43 percent requires heat over 400 ºC.

The use of solar energy to supply thermal requirements in industrial processes is an environmental friendly alternative applicable to different industrial sectors. However, there is still much room for innovation which has been largely unexploited. In several countries, chemical, petrochemical, textile, food and beverage industries have been considered to assess the substitution of conventional fuels by solar energy, although such a development is still in research stage (Baniassadi et al., 2015). Other promising sectors considered in literature include paper, mineral products, wood, tobacco and machinery among others (Lauterbach et al., 2012). Most studies aimed to integrate thermal solar energy as industrial heat process have been done on below 100 ºC and 100-400 ºC temperature ranges (Calderoni et al., 2012; Frein et al., 2014). Nevertheless, the feasibility of using solar industrial process heat at high and extremely high temperatures has been studied only for small scale processes such as synthesis of chemicals and materials treatment (Steinfeld et al., 2001). (Calderoni et al., 2012). The latest developments in concentrating solar energy technologies tend to increase

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the operation temperature in order to improve thermal conversion efficiency. If temperatures higher than 1000 ºC are reached in large scale systems, other industrial processes such as some metallurgical reactions can be considered to be addressed with solar thermal energy.

The general challenge in the field is a proper integration of state of art solar thermal technologies according to the heat, temperature and transfer medium requirements. Economic arguments must be also taken into account: due to relatively low energy prices for industrial customers in several countries worldwide, solar thermal systems do often have pay-back times higher than their lifetime. In general, the heat is transferred through a heat transfer medium (water, steam, air, etc.). For those processes that need constant loads, thermal storage and/or fossil hybridization have to be considered.

The lead–acid battery (LAB) is one of the most recycled products throughout the world with a recycling rate in most countries exceeding 95%. Because LAB dominates consumption of the element, around 80% of world lead output, secondary lead sourced from batteries is the major contributor to the world's annual lead production of around 8.4 million tons (Stevenson, 2009). Recycling contributes to the minimization of environment pollution and the conservation of natural lead resource. Moreover, it is considered a profitable business because of the value of lead as a commodity ("Lead Recycling Sustainability in action," 2014) and currently is cleaner and safer thanks to the lasts regulations.

Although the traditional high pollution associated to LAB recycling plants is being decreased with the more recent developments, their high energy consumption is still environmentally harmful. Frías et al. (year not available) presented an innovative process to reduce global pollution in LAB recycling (Frias et al., year not available.). Although their proposal is cleaner than more conventional technology, it still consumes 1 MWh/t Pb. As with other industrial processes, thermal solar energy could be employed to provide heat to several stages of the recycling plant. Thus, the objective of this work is to carry out a preliminary assessment of the potential to integrate central receiver solar thermal technology as heat source for the recycling process, considering two different scenarios: Spain and Chile. More than 350000 tons of LAB are processed in Spain annually what means more than $1.40 \cdot 10^{11}$ kJ of heat consumption in the form of natural gas. On the contrary, the industry in Chile is much smaller, with around 25000 tons of batteries annually recycled. The availability of solar resource is also quite different in both countries, as shown in the corresponding section below.

## 2. Methodology for the potential assessment

In order to assess the potential use of thermal solar energy in the LAB recycling industry, a general description of the process is presented based on different sources of bibliography and several visits to the plants of Exide Technologies (San Esteban de Gormaz, Soria) and Recobat-Lyrsa (Albate del Arzobispo, Teruel) in Spain, as well as personal communications from the qualified staff of these companies.

A simplified scheme of the operations retained for the study is presented. Typical operation temperatures and distribution of heat demand per ton of produced lead are stablished. The medium through which the heat is supplied is also informed. Those processes that occur at high temperature are selected and solutions are proposed based on the integration of solar central receiver technology. Different thermal storage technologies are also taken into account for the analysis.

An overview of the LAB recycling industry situation in Spain and Chile is also presented. Because the volume of processed LAB is very different in the two countries, two different plant sizes are selected for the study according to both scenarios. Situation of the plants in Chile and Spain are selected among the locations of existing plants, taken into account the isolation conditions.

Assuming that the industries have a portion of available land in their neighborhood, where a solar plant could be installed, a solar field is dimensioned to supply heat to the recycling process. To do that, DNI data of Spain are taken from Meteonorm. Because such a database does not include some areas of Chile, DNI data of Chile are taken from measurements published by the Energy Ministry of Chile. Once the heliostat field and the receiver are dimensioned for the established cases, including a certain solar multiple and a storage capacity, the energy production is monthly calculated. Then, the annual solar fraction is also given.

## 3. Description of the industrial process

Recycling of spent LAB to obtain secondary lead involves several stages of a global process from the reception of the batteries to the final production of the lead. In general, recovery of the lead and other components is not difficult because the batteries are easily broken and divided into their various fractions. Thus, the recycling of LAB is well established practice throughout the world (Stevenson, 2009).

Although there is not a unique scheme but a combination of different alternatives, many countries have implemented similar recycling technologies able to maintain recycling rates greater than 90%. Stevenson (2009) offers an overview of the most common procedures. Once received at the recycling plant, a LAB undergoes several breaking operations. Free sulfuric acid is drained and pumped to a neutralization plant. The battery itself is dismantled through a hammer mill or roller crusher. The plastic fractions are usually separated by floatation. Other processes exit to separate the components of a LAB, such as using a saw to remove the plastic top and a trommel to extract the internal metallic fractions. The internal parts of a LAB are composed of small fractions of metals and other materials and mainly of the so-called paste, which is formed by the positive (lead oxide, 30-35 %) and negative (lead sulfate 55-60 %) active materials of the battery. The plastic fraction is composed of polypropylene and polyethylene and, to be recycled, it is required their melting at temperatures that varies between 150 and 200 ºC, depending on the fraction composition. Hot air is usually employed as heat transfer medium. Some batteries recycling plant do not include this process but they send the plastic to be recycled elsewhere. Two methods exist for the recovery of lead from battery paste, grid and other lead components; pyrometallurgical and hydrometallurgical. Pyrometallurgical are the dominant methods for both recovery and refining and they are particularly taken into account in this analysis because of their high demand of heat. Main pyrometallurgical operation is the smelting of the grids and active materials, which usually takes places in rotary kilns that are also loaded with iron, coke and other compounds as silica and sodium carbonate (Zabaniotou et al., 1999). The exact composition of kilns load depends on the desired composition of the final product. In general terms, two types of finished lead can be differentiated: one of higher purity (99.98%) that will be further employed to produce lead oxides for cathodes and another one, of lower purity, called hard lead (~97%) that will give rise to grids and the production of lead sulfates for anodes (Zhang et al., 2016). Furnaces temperature can vary in a range of 950-1100 ºC depending on the load. Exhaust gases are employed to preheated air that enters in the kiln at 400-500 ºC. Then, internal temperature of the kiln is increased through natural gas driven burners. After the smelting, lead is separated from the slag and conducted to refining stage. A kettle is operated at maximum temperature of 650 ºC although its temperature varies depending on the consulted source and the finished product composition. Different substances are also added in this stage, such as NaOH, NaCl or $NH_3NO_3$. The result from the refining operation is the commercial pure or hard lead. A general flowsheet of the recycling processes is shown in Figure 1. Although the plants usually operate 24 hours a day, the process is not always continuous. Thus several intermediate storages can be found between one stage and the next.

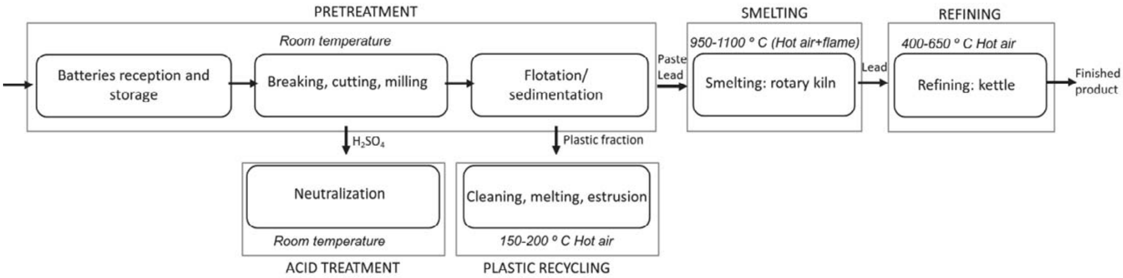

**Fig. 1: Flowsheet of a typical lead-acid batteries recycling plant including the most common operations and working conditions.**

## 4. Definition of the study

### *4.1. Heat demand*

Because plastic fraction is usually send elsewhere for its recycling, it is not considered in this analysis. Then, the operations retained for this assessment work at temperature ranges characteristic of solar tower CSP systems.

Smelting temperature can vary between 950-1100 ºC and it is assumed as the average in this case: 1025 ºC. Rotary kilns employ natural gas burners and the heat consumption can be estimated in 43 $m^3$ per ton of finished product. Refining temperature can be also variable in a significant range but it is considered of 525 ºC for this preliminary analysis. Gas natural consumption of a typical kettle can be estimated in 18 $m^3$ per ton of finished product. Considered net lower calorific value of natural gas is 10.83 $kWh/Nm^3$. Note that the furnaces, both rotary and kettle, usually perform in batch mode, what implies the need of storing the material before each operation. Nevertheless, the furnaces are expected to operate also during nights, so for a preliminary analysis it can be considered a constant heat demand 24 hours a day all year round. Thus, thermal storage must be included in the analysis. These definitions are particularly stablished to carry out this work. Although they do not correspond with realistic data of any particular plant, they are based on the information provided by Exide Technologies and Recobat-Lyrsa.

### *4.2. Location, plant size and solar resource*

LAB recycling is an extended practice in Spain with more than 350000 tons of batteries annually processed. (Gallardo Gómez, 2014). This represents a recycling rate over 95% but involves more than $1.40 \cdot 10^{11}$ kJ of heat consumption in the form of natural gas. It is important to note that primary lead production is null in Spain. Four important recycling plants are distributed in different locations of the country and they are indicated in Figure 2 together with their capacity in tons of lead annually produced. Other plants of less capacity are located around the country. The present study is based on a plant located in Murcia which capacity is defined in 30000 tons of lead per year. Murcia is one of the locations of higher DNI as it can be observed in Figure 2 (Geomodel, 2014, 2015).

The LAB recycling industry in Chile is much smaller, with around 25000 tons of batteries annually recycled. Many of the Chilean spent LAB are exported to other countries, mainly to Peru. For instance, 14000 ton of spent batteries were exported in 2008 to several countries. Moreover, there are a significant number of non-authorized recyclers that process batteries outside the law (Gobierno de Chile and GTZ, 2009). Figure 2 shows the location of the only authorized plant that currently operates in Chile whose capacity is about 8000 tons of end lead per year. It is placed in Calama, in the middle of the Atacama Desert where the insolation is the highest measured in the world. This plant is the reference for the definition of the Chilean cases.

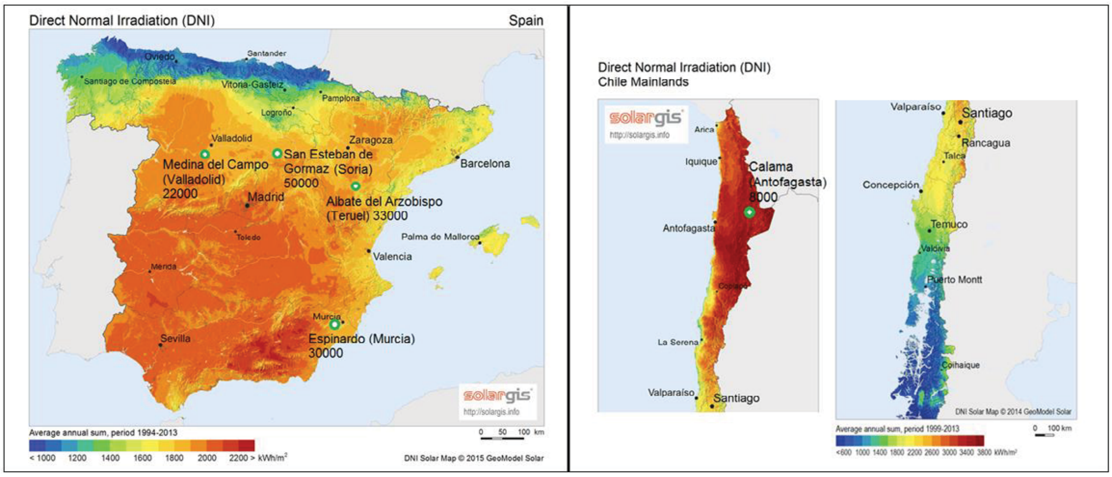

**Fig. 2: DNI maps of Spain and Chile provided by SolarGis. Location of the main plants of lead-acid batteries recycling in Spain and Chile (indicated with a green circle) and their approximate capacities in produced tons of end lead per year.**

### 4.3. Cases of study

Smelting and refining operation in both countries, Spain and Chile, have been selected as cases of study. Central receiver technology could be coupled with the processes according to the temperature values. Refining operation could be also coupled with a parabolic through plant but it is not analyzed in this work. Table 1 compiles the specific problems that are approached in this study. Combinations of different plant size, location and point of application in the industrial process leads to four cases of study. Heat demands are estimated for each case taken into account the selected plant capacity and the consumption previously defined for each operation.

**Table 1. Definition of starting conditions for the present study. Four cases have been selected by combining different applications, location and plant size.**

| Case | Location | Operation | Heat demand (GWh/y) | Temperature (ºC) |
|---|---|---|---|---|
| 1 | Murcia (Spain) | Smelting | 14 | 1025 |
| 2 | Murcia (Spain) | Refining | 5.8 | 525 |
| 3 | Calama (Chile) | Smelting | 3.7 | 1025 |
| 4 | Calama (Chile) | Refining | 1.6 | 525 |

## 5. Analysis of proposed cases

### 5.1. Case 1

A field of heliostats with an air central receiver can be considered for this case. Since the heat demand is 14 GWh/y and a constant demand is assumed, the required net thermal power is 1.6 MW. A high solar multiple has to be considered in order to overproduce a considerable amount of energy to supply such constant demand. A 3.5 is the selected value for this case and the following for comparative purposes. A storage capacity of 18 h is considered for calculations. Note that the storage capacity will be decreased according to the thermal storage system efficiency, which will depend on the TES system, but it is neglected for this analysis. This solar multiple lead to a receiver useful power of 5.6 MW and this value defines the plant size. For this power, one side oriented heliostats field coupled with a volumetric receiver could be used. In volumetric receivers airs flows through a porous structure and it is heated to high temperature. Ceramic volumetric are suitable to achieve up to 1200 ºC. The system may require a CPC when the peak concentrated solar flux is not sufficient to reach the process temperature. A typical efficiency of a ceramic volumetric receiver is taken from the average of the examples published by (Ávila-Marín, 2011) and it is 64%. Considering an efficiency of the heliostat field of 70 % (Falcone, 1986) for a conservative estimation, the required area of collection would be 12537 m$^2$. For this calculation, the maximum annual DNI of Murcia (997 W/m$^2$) was used. Advanced TES systems should be taken into account to be coupled with this type of solar plant. High temperature thermochemical storage (TCS), which is still in development stage, would be suitable to storage and release heat at temperatures ranges of 800-1200 ºC, depending on the employed material. Many works on such a topic can be found on literature (Agrafiotis et al., 2015; Alonso et al., 2015; Pardo et al., 2014)

### 5.2. Case 2

For this case, a one side oriented heliostat field combined with a central receiver is also selected. Because of the temperature range, this application can be easily coupled with more developed technologies: a cavity with a tubular receiver and the so called Solar Salt (60 % $NaNO_3$, 40% $KNO_3$) as thermal fluid. The heat demand is 5.8 GWh/y and for a constant demand, the required net thermal power is 0.74 MW. The efficiency of the receiver belonging to PS10 plant (Spain) is taken as a reference, which is close to 90% (Siva Reddy et al., 2013). Although this plant works with water as thermal fluid, the type of receiver can be coupled with the here exposed case. The considered heliostat field efficiency is 70%. A solar multiple of 3.5 is also included in this case as well as 18 hours of thermal storage, using for that a two tanks molten salts storage system, which is the most commercially developed currently. Thus, receiver power is set in 2.6 MW. The required collection area, calculated with the maximum DNI in Murcia results of 4139 m$^2$.

### *5.3. Case 3*

Case 3 can be analyzed in a homologous form than Case 1. A one side oriented field of heliostat and a volumetric air central receiver are the technologies suitable to be integrated with the smelting operation. Constant heat demand is 3.7 GWh/y, that is, a power requirement of 0.4 MW. Assuming the same criterion to select the solar multiple, the receiver size would be 1.5 MW. The system may require a CPC when the peak concentrated solar flux is not sufficient to reach the process temperature. In comparison with the plant proposed in Case 1, better efficiencies of the heliostat field and volumetric receiver could be assumed due to the favorable climatic conditions of the plant location. A deeper analysis on the design parameters would be required to achieve a relevant evaluation. However, for this preliminary assessment, 70% and 64% are considered as heliostat field and receiver efficiencies respectively. The resulting collection area, for the maximum annual DNI in Calama (1132 W/m$^2$) is 2958 m$^2$.

### *5.4. Case 4*

Case 4 would be equivalent to Case 2 in the employed technology and to Case 3 in the location and therefore, the climatic conditions. Proposed technology is a cavity with a tubular receiver coupled with a one side oriented field of heliostats. Thermal fluid would be molten salts (Solar Salt) as shown in Case 2 and it would be included a two-tanks thermal storage system able to take profit of the sensible heat of such molten salts. Constant heat demand is 1.6 GWh/y, that is, a power requirement of 0.18 MW. With a solar multiple of 3.5, the receiver power would be 0.63 MW. Receiver and heliostats field efficiencies taken for this case are 90% and 70% respectively. Then, the required collection area, calculated with the maximum DNI in Calama results of 918 m$^2$.

## 6. Annual energy supply

In this section, the annual energy supply estimated to each one of the previously analysed cases is presented. Figure 4 depicts the energy monthly produced according to the designs proposed in section 5. In Case 1, 68 % of the annual energy demand could be supplied by the solar plant, while 32 % should be provided by means of a fossil fuel source of energy. Thus, a hybrid installation will be required despite the use of thermal storage. A re-dimensioning of the plant could be interesting taking into account the cost of both the thermal storage and the fossil fuel back-up. Similar analysis can be done for Case 2 where 76 % of the annual demand could be covered by the solar plant. On the contrary, because of the favourable climatic conditions, those plants located in Calama would have a production close to the annual heat demand of the proposed industrial process. Calculations for Case 3 indicated the plant produce 90 % of the annual required energy, while result for Case 4 is 94 %. The production of a solar plant in Calama is more constant than in Murcia, which is favourable to be combined with a constant demand industrial process.

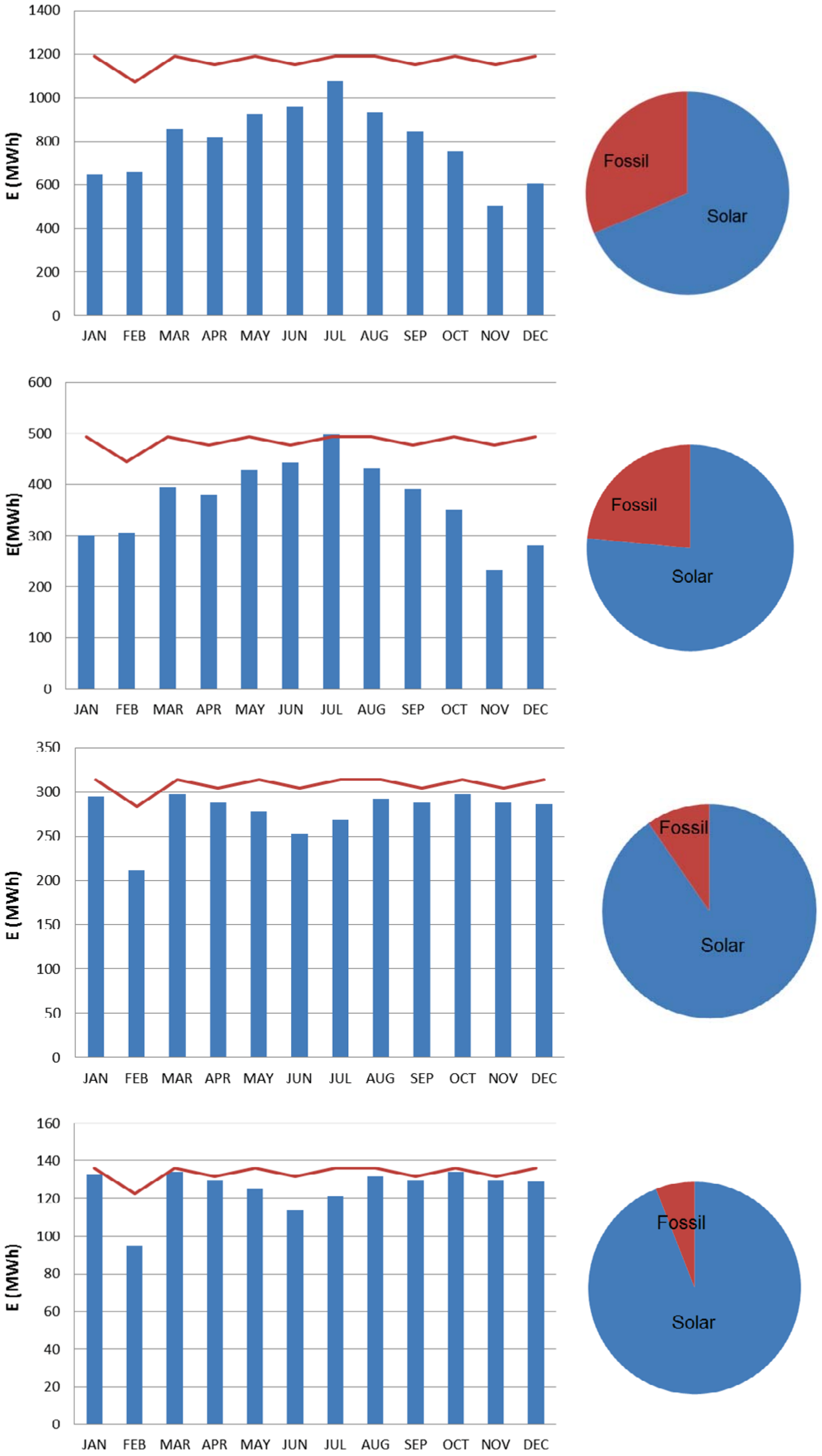

**Fig.3. Energy production by the plants dimensioned to the cases described in section 5 per month during a typical year (case 1, 2, 3 and 4 respectively). Red line indicates the monthly heat demand. Fraction of the heat demand that should be provided by conventional fuels, according to the proposed designs.**

## 7. Conclusions

Lead acid batteries (LAB) recycling industry is a strong sector all over the world and the associated heat demand is very significant. A preliminary analysis of the opportunities to integrate CSP technologies in the LAB recycling industry is presented in this work. Two operations, smelting and refining are retained for a concrete analysis and they are couple with central receiver technology. Two different locations are studied: Murcia (Spain) and Calama (Chile), with different climatic conditions. Thermal storage is considered by giving a solar multiple and a storage capacity. Using typical data of literature for plant dimensions estimation, the annual solar fraction of energy demand is obtained for the four proposed cases. While in Spain the proposed solar plants are able to supply 68 and 76% of the smelting and refining respective annual demands, in Chile the solar fraction achieves 90 and 94 %. The production of a solar plant in Calama is more constant than in Murcia, which is favourable to be combined with a constant demand industrial process. Economic aspects as well as daily energy supply management must be taken into account in a further stage for a more complete analysis.

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