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Life Cicle Inventory for Lead Azide Manufacture

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ABSTRACT: Like any other manufactured chemical compounds, explosives are produced using chemical reactants and other utilities (steam, heat, compressed air, feed water and electricity) and generate a set of environmental impacts (waste water, solid and water residue and waste heat, for example). On top of that, one can count the intrinsic hazard characteristic of explosives and the possibility of accidents involving these compounds. Within this framework, explosives present themselves as chemical compounds suitable for both LCI (Life Cycle Inventory) and LCA (Life Cycle Assessment). This LCI study takes into account all the raw materials, utilities and wastes taking place during the production process. In this particular article, lead azide has its processed mapped and inventoried under the scope of ISO 14040. ISO 14040:2006 describes the principles and framework for life cycle assessment (LCA), including: definition of the goal and scope of the LCA, the life cycle inventory (LCI) analysis phase, the life cycle impact assessment (LCIA) phase, the life cycle interpretation phase, reporting and critical review of the LCA, limitations of the LCA, the relationship between the LCA phases and conditions for use of value choices and optional elements. The Lead azide was chosen due its singular explosive characteristics (very sensitive, which makes lead azide the explosive of choice as a primer in several applications. The results and conclusions of this study are drawn from the review of the process, its analysis, as well as from the application of life cycle inventory methods upon the manufactory of lead azide, a highly sensitive primer explosive, providing solid ground for the further studies, such as a full LCA assessment. Furthermore, for explosives, most LCA research works aims towards disposal, not addressing manufacturing, which is the main strength of this work.

KEYWORDS: Lead azide, Manufactory process, Life Cycle Inventory, Life Cycle Impact Assessment, Life Cycle Assessment.

INTRODUCTION

Explosives are chemical compounds capable of undergoing a very rapid decomposition (detonation), which generates heat and produces gases, which can be converted in usefull work (thermodinamically defined). Overall, explosives have many applications, ranging from military to civilian. While the military applications of explosives are straightforward in its nature (bombs, mortars, missiles, payloads, for example), the quantities of explosives destined to the civil applications are significantly larger, due to its usage in infrastructure (mining operations, oil extraction and demolitions, for example).

Like all other manufactured chemical compounds, explosives are produced using chemical reactants and other utilities (steam, heat, compressed air, feed water, and electricity) and generate a set of environmental impacts (waste water, solid and water residue and waste heat, for example). On top of that, one can count the intrinsic hazardous characteristic of explosives and the possibility of accidents involving these compounds. Within this framework, explosives present themselves as chemical compounds suitable for LCI (Life Cycle Inventory) and LCA (Life Cycle Assessment) studies.

This study is a LCI and takes into account all the raw materials, utilities and wastes taking place during the production process. Hence, in this particular study, lead azide was the chosen explosive to have its manufactory process studied. Lead azide was chosen due to its explosive characteristics (very sensitive, which increase risks of detonations but makes it a mandatory compound in almost every explosive use), intense use and the presence of lead in the raw materials (in the form of lead nitrate) and residues.

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Therefore, for this article, the manufactory process of lead azide was mapped using the fundamentals of ISO 14044, qualitatively analysed and had its environmental impacts identified and categorized (midpoint and endpoint). ISO 14040:2006 describes the principles and framework for life cycle assessment (LCA) including: definition of the goal and scope of the LCA, the life cycle inventory (LCI) analysis phase, the life cycle impact assessment (LCIA) phase, the life cycle interpretation phase, reporting and critical review of the LCA, limitations of the LCA, the relationship between the LCA phases and conditions for use of value choices and optional elements. ISO 14040:2006 covers life cycle assessment (LCA) studies and life cycle inventory (LCI) studies. It does not describe the LCA technique in detail, nor does it specify methodologies for the individual phases of the LCA.

Furthermore, for explosives, several LCA works (Alverbro *et al.*, 2009; Hochschorner *et al.*, 2006; Hochschorner and Finnveden, 2006) aim towards disposal and applications, not addressing manufacturing, which is the focus of this study.

This study aims to disclose the life cycle inventory of a largely used primary explosive (lead azide), aiming to help other researches addressing the environmental impacts in manufacturing lead azide, as well as other lead-based explosives. Thus, this study aims to review one of the processes for manufacturing lead azide, as well as to build the life cycle inventory of the overall process as a preparation for modelling the life cycle of lead azide manufacture.

BACKGROUND INFORMATION

This section provides useful background regarding LCA, explosives, lead azide and its manufacture processes.

LIFE CYCLE ASSESSMENT (LCA)

Sonnemann and Castells (2004) presents a list of some analytical tools for environmental managing, in which LCA ranks first as a standardized method for product-oriented environmental impact assessment (ISO 14001; ISO 14040; ISO14040:2006; Zharen, 1998). Alverbro *et al.* (2009) defined Life cycle assessment (LCA) as a method for assessing the potential environmental impacts and resources used throughout a product's life from raw material acquisition, production, use and waste management (ISO 14040:2006). It is important to determine that, under ISO, the term 'product' can also include services such as waste management.

The purpose of the LCA study of a particular product is to identify the main environmental impacts caused by the product or service evaluated to better determine the actions required for mitigation of impacts. According to ISO 14.040:2006, the steps of LCA are: goal and scope definition, inventory analysis, impact assessment, and interpretation. Modern work (Clift *et al.*, 2000) stated that LCAs are commonly carried out to compare alternative ways of delivering some function. The basis for comparison, common between all alternatives, is termed the Functional Unit for the study.

LIFE CYCLE INVENTORY

Life cycle inventory is a part of larger initiatives towards environmental management (ISO 14001; Zharen, 1998) under the guidance of ISO standards such as ISO 14001, ISO 14040 and ISO 14040:2006. To perform a life cycle inventory, it is necessary to determine inputs and outputs within a given system, collect data as well as looking at environmental aspects. According to recent work (Haddad *et al.*, 2013), a LCI study must be carried out for each subsystem involved, materials and energy, generation of products and by-products, as well as pollutants. This inventory is known as LCI. Furthermore, as addressed by Passer *et al.* (2012) for an environmental construction, LCI is one step prior to the a full LCA. While the LCA aims to determine an indicator that assesses key environmental aspects, the LCI aims to obtain a condensed and reliable array of data.

EXPLOSIVES OVERVIEW

Explosives are substances of great importance in the human development, being applied in many key areas, such as in the oil industry (Galante *et al.*, 2013). In addition to its traditional use in the military industry, it is usage is noticeable in great engineering projects, such as the construction of tunnels and exploitation of natural resources, like mining and oil exploration. Explosives are chemical substances or mixtures of substances that react rapidly by heating or attrition, generating huge volumes of gas and heat. The general formula for an explosive is $C_xH_yN_wO_z$ (Kinney and Graham, 1985). Explosives can be classified by several standards; however, the most common way of classifying explosives is according to its detonation velocity and activation energy. Table 1 presents a classification matrix with some examples.

Table 1. Explosives Classification matrix (compiled by Authors).

		Classification due to detonation velocity	
		High explosive	Low explosive
Classification due to activation energy	Primers	Lead azide	Lead styphnate
	Boosters	RDX, TNT, HMX	Gun powder Black powder

In general, to allow a full detonation to occur, a set of different explosives is required. The simplest configuration starts with a primer, which is ignited by spark, friction, flame or impact and provides energy to ignite other more powerful explosives. Among the primers, lead azide can be counted as the most used both in military and civilian applications.

THE LEAD AZIDE - PRIMER EXPLOSIVE

The lead azide is an explosive initiator, being more efficient than mercury fulminate. It requires a higher temperature for spontaneous combustion and does not decompose during long storage periods at moderately elevated temperatures. When compressed into a capsule, lead azide ignites detonating or exploding the spark (Ramaswamy *et al.*, 1981), but not as immediately as mercury fulminate. For this reason, the main charge initiation of a blasting cap composed of $Pb(N_3)_2$ is generally mixed in defined proportions with lead styphnate or other sensitizers to cause the explosion more easily, though with a less violentflame, which serves to initiate the explosion of azide.

The sensitivity to shock and friction rapidly increases in proportion as the particle size increases. Crystals of 1 mm in length are subject to a spontaneous explosion due to the energy content that they possess. Lead azide should not have needle-shaped crystals with a length greater than 0.1 mm. Lead azide with dextrin may appear to be safely stored under water for a long time. However, there is a belief that crystallized azide becomes more sensitive when stored under water due to an increase in the size of the crystals. Lead azide is produced in two crystal forms: orthorhombic (α), density 4.71 and monoclinic (β), density 4.93. The formation of the orthorhombic form, very sensitive, prevented the mixture of a diluted solution of lead nitrate and sodium azide, with which lead azide is prepared (Allan *et al.*, 1963; Imbel, 2013; Leslie, 1966).

Lead azide with dextrin can be soluble in cold water to extent measure of 1% because of the presence of dextrin. Both forms are almost insoluble in ether and acetone. Ethanol has little cold solvent action on the product and lead azide can be stored when wetted with a mixture of equal volumes of water and ethanol. Lead azide is soluble in aqueous solutions with ammonium acetate 10%. When exposed to an atmosphere with 90% of relative humidity at 30°C, lead azide in crystal form is hygroscopic and coated with a measure of 0.03 and 0.8%, respectively, of dextrin (Akhavan, 2011; Allan *et al.*, 1963; Cooper, 1996; Holloway *et al.*, 1965; Leslie, 1966; Meyer *et al.*, 2007; Urbanski, 1984). Dry lead azide does not react with or corrode iron, steel, nickel, aluminium, lead, zinc, copper, tin or cadmium. Coatings of acid-proof black ink, shellac or iron surfaces, do not show any effect. In the presence of moisture, it corrodes copper and zinc and, in the latter case, it forms the dangerous and highly sensitive copper azide. For this reason, lead azide is not loaded or placed in contact with uncoated copper or their alloys (bronze, brass and other metals) (Silva and Iha, 2010; Urbanski, 1984).

Lead azide is obtained as a white precipitate, by reaction of a solution of sodium azide in a solution of lead acetate or lead nitrate. It is absolutely necessary that the process be conducted so that the precipitate formed creates very very small crystals. There are several approaches to the manufactory process. Lead azide manufactory is well known in technical literature (Leslie, 1966) and can be obtained with dextrin (Allan *et al.*, 1963; Holloway *et al.*, 1965) or without it. From Meyer *et al.* (2007) as well as other sources (Akhavan, 2011; Cooper, 1996; Date *et al.*, 2009), one can design the process for dextrinated lead azide as presented in Fig. 1.

A standard plant that is able to hold a production unit as described in Fig. 1 contains vessels for the preparation of solutions (mainly solutions of sodium azide and lead nitrate), jacked vessels for the precipitation of lead azide, as well dosing pumps, filtering and drying installations. Due to the standard reaction using lead nitrate in excess, the wastewater is full of lead, and requires treatment before the final disposal. This treatment can be carried out using precipitation or other methods (like ionic resin). Since the simpler method is precipitation using sulphate, this study considers it in the inventory.

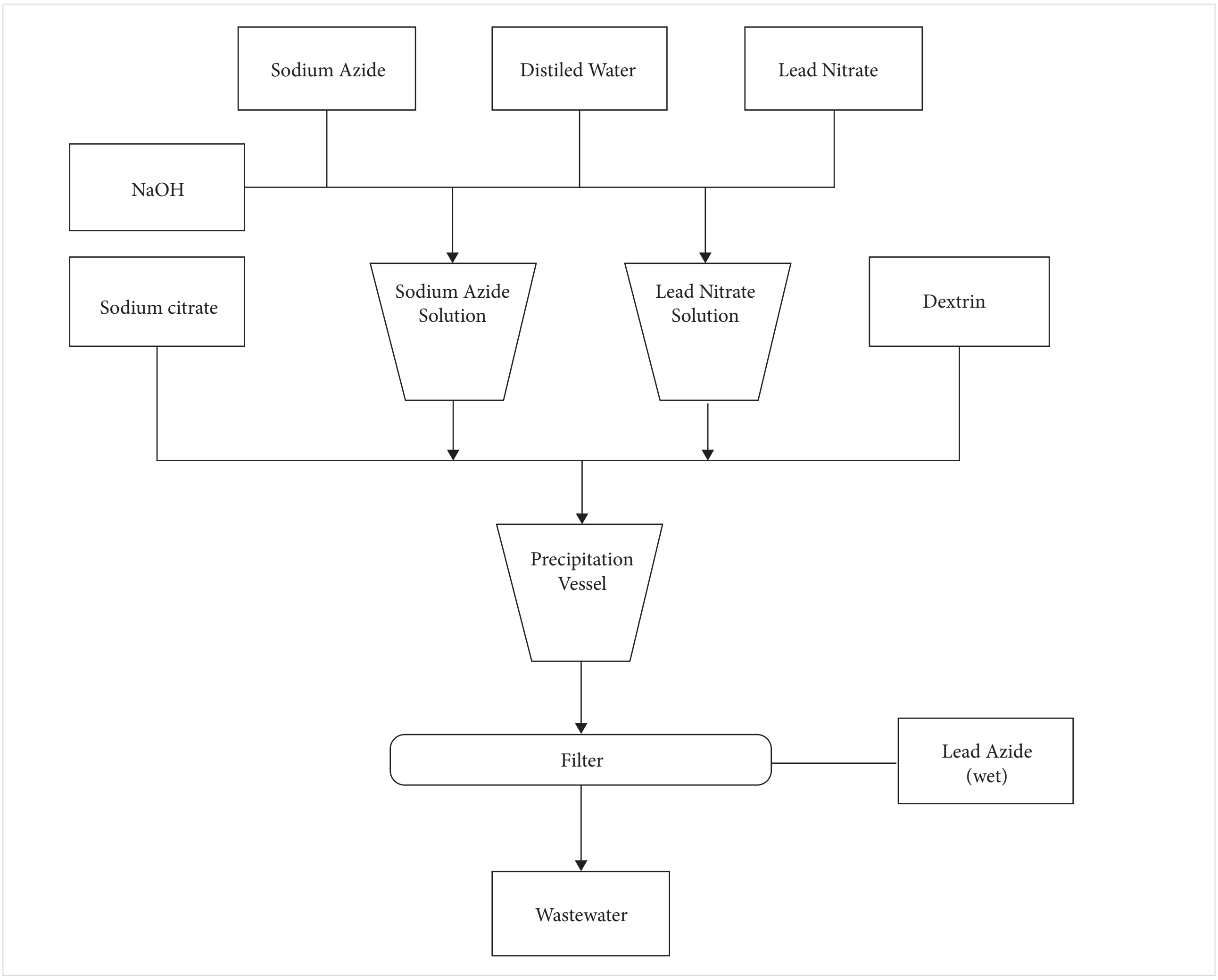

Figure 1. Manufactory process for lead azide (based on (Allan *et al.*, 1963; Holloway *et al.*, 1965; Imbel, 2013; Leslie, 1966)).

The steam generator consists of a set of equipment for producing water vapour. The water vapour produced is intended to distil the water from the solution, heating the reactive mixture and drying the lead azide produced.

LEAD AZIDE: LIFE CYCLE INVENTORY

The mapping starts with the identification of the manufacturing process and inventory stages of raw material inputs, energy inputs and service inputs themselves or other factors that may cause environmental impacts. With these data, enough information can be collected to understand the situation, qualitatively and quantitatively.

In the following sections of this chapter, the parameters of the four stages of the the manufacturing process life cycle of lead azide are defined, according to the goal and scope defined by ISO 14040:2006, from the inventory analysis of the life cycle assessment, life cycle impact and interpretation of the life cycle. This inventory was compiled from the processes described by (Allan *et al.*, 1963; Holloway *et al.*, 1965; Leslie, 1966) and used by (Imbel, 2013).

PRODUCTION SYSTEMS

The main part of the production system under study consists of both phases directly and indirectly linked to the production process of lead azide, as presented in Fig. 1. The operation and procedures taking place can be folded into subsystems. Each subsystem is described, quantified, analysed and summarized in Table 2.

Table 2. Subsystems for production of lead azide.

Subsystem	Description of the operation
Subsystem for the production of sodium azide	The production starts with 450 L of water (free of impurities and salts) being placed in a plastic container, in which are dissolved 4.9 kg of sodium azide with manual stirring. The pH of the solution is checked; if other than 10, 1.5 L of sodium hydroxide solution 14% are added. After this, it is linked to continuous stirring for several minutes, and then the solution is ready.
Subsystem for the production of lead nitrate	The production starts with 450 L of water (free of impurities and salts) being put into a plastic container, in which are dissolved in 33.7 kg of dried and crystallized lead nitrate. After that, the solution is stirred for several hours and allowed to sit for 8 h. The density of the solution should be 1.05 g/cm^3 and the pH should be between 5 and 6 before being transferred by gravity to the intermediate reservoirs.
Subsystem for the production of sodium hydroxide	For this solution, 1.4 kg of sodium hydroxide are dissolved in 10 L of water under agitation.
Subsystem for the production of dextrin aqueous solution	The coating agent (dextrin) is dissolved in filtered water at a proportion of 2 kg of agent for every 5 L of water. The solution is placed under heating (100°C) for 4 h with manual stirring every 30 min. After that, the solution must be cooled naturally and the density should be 1.154 g/cm^3.
Subsystem for the production of lead azide	The reactor is fed manually with 6 L of the lead nitrate solution prepared above; this is measured on a solution of sodium azide at a rate of of 5L/40min. During the reaction, it should be kept under constant stirring, heated to 80°C and 50mL should be added to the corn-starch dextrin solution. After the end of the dosage of sodium azide, the circulation of hot water is closed in the reactor jacket and the solution is allowed to sit for 1min. After this, the supernatant mother liquor is poured into a plastic container and the precipitate - lead azide - is filtered on a Büchner–Kitassato flask with the vacuum turned on. 500 ml of ethyl alcohol GL 96% are added to the ending process of the already filtered lead azide in order to optimize the drying process of the product.
Subsystem for effluent treatment	15 L of a sulphuric acid solution 50% are inicially placed in the tanks of the treatment plant. Then, the mother liquor effluent from each reaction is added and 1 L of a sodium nitrite solution 7% is added to the 2 cargo tank poured into the effluent. Sodium nitrite is explosive, and a distortion of the sulphuric acid precipitation is in the form of lead sulphate. The tank of the treatment plant may receive up to 12 loads of effluent, 6 L of sodium nitrite and 15 L of sulphuric acid. There is no stirring or heating. All of the loading and unloading of the solutions is done manually.

The following subsystems are indirectly linked to the cycle of the manufacturing process of lead azide, but were not included in this study:

- Production of fuel oil (boiler fuel);
- Production of electricity;
- Condensing of steam for use of process water;
- Production of steam;
- Manufacture of sodium azide;
- Port logistics (because the company model sodium azide is an imported product);
- Manufacture of lead nitrate;
- Manufacture of dextrin;
- Manufacture of sodium citrate;
- Manufacture of sodium hydroxide;
- Manufacture of ethyl alcohol 96% GL;
- Transportation: sodium azide, lead nitrate, corn-starch dextrin, sodium citrate, sodium hydroxide and ethanol 96% GL.

PRODUCT FUNCTION AND FUNCTIONAL UNIT

The product function is to allow the explosive lead azide to load fuses, a primer accessory used for initiation of the explosive train. Due to its high sensitivity, it is not necessary for bulk loading of the primer. The functional unit for the development of the study was fixed at 1.0 kg of lead azide produced. This value is the basis for the standardization of data in the preparation stage of the Life Cycle Inventory.

SYSTEM BORDERS

The product system is related with environmental aspects by the following steps: Consumption of natural resources (direct): crude oil and water; Energy consumption: electricity and fossil fuels; and Generation of waste: atmospheric emissions, liquid effluents and solid waste. A full set of borders and subsystems included in the study, as well as the excluded, are listed in Table 3.

SYSTEM BALANCES

From information, it is possible to consolidate inputs and outputs for each subsystem. These results are presented in Table 4.

Further analysing the subsystems (Table 4), it was necessary to determine the quantities of each raw material involved in the production of one kilogram of dry lead azide. This information is presented in Table 5, which was compiled using processes described by several sources (Allan *et al.*, 1963; Holloway *et al.*, 1965; Leslie, 1966) and under production in some industries (Imbel, 2013).

Furthermore, it is possible to determine that the two main raw materials are sodium azide and lead nitrate. Sodium azide, being a salt is not hygroscopic. It can be white or yellow. Its density ranges from 1.846 at 20°C in 100 parts of water to 40.7 at 15.2°C in parts of dissolved sodium azide. It is insoluble in ether and 100 g of absolute ethanol at 0°C can dissolve 0.22 g of sodium azide. The aqueous reaction is basic. When heated on a metallic plate, it does not melt, remaining unchanged up to 350°C, and detonates at higher temperature. When heated in vacuum, it decomposes into Na and N_2.

Table 3. Summary of the borders and limitations.

Subsystems considered	Subsystems outside this study
- Subsystem for the production of sodium azide - Subsystem for the production of lead nitrate - Subsystem for the production of sodium hydroxide - Subsystem for the production of dextrin aqueous solution - Subsystem for the production of lead azide - Subsystem for effluent treatment	- Production of fuel used for steam generation - Production of electric energy; - Production of steam - Manufactory of sodium azide - Manufactory of lead nitrate - Manufactory of dextrin - Manufactory of sodium citrate - Manufactory of sodium hydroxide - Manufactory of alcohol - Port logistics and transports

Lead nitrate is a salt of colourless crystals. It begins to decompose at 200°C, giving off gaseous nitrous oxide and lead. It is soluble in water. Lead nitrate is much less hygroscopic than the other nitrates, except potassium nitrate. While the

Table 4. Subsystems balances.

Subsystem	Input	Output	Product
Subsystem for the production of sodium azide	Sodium azide (powder) Process water Electricity	Heat	Sodium azide 99%
Subsystem for the production of lead nitrate	Lead nitrate (powder) Process water Electricity	Heat	Lead nitrate 98%
Subsystem for the production of sodium hydroxide	Sodium hydroxide (powder) Process water Electricity	Heat	Sodium hydroxide 93%
Subsystem for the production of dextrin aqueous solution	Dextrin Process water Electricity Heat	Heat	Dextrin (solution)
Subsystem for the production of lead azide	Ethanol 96% GL Sodium azide 99% Sodium citrate Sodium hydroxide 93% Dextrin Lead nitrate 98%	Heat Wasted water (with high concentration of lead)	Lead azide
Subsystem for effluent treatment	Waste water (with high concentration of lead) Sulphuric acid	Waste water (contaminated with diluted lead)	Lead sulphate

Table 5. Material balances.

Raw materials	Quantities
Ethanol 96% GL	0.84 L
Sodium azide 99%	0.51 Kg
Sodium citrate	trace
Sodium hydroxide 93%	0.01 kg
Dextrin	0.07 kg
Lead nitrate 98%	1.38 Kg

alkali nitrates and alkaline clay turn intoexplosion carbonates or oxides, lead nitrate's boiling point is at about 160°C. Lead nitrate, similarly to ammonium, has the property of being completely volatile, although only at high temperatures.

ENVIRONMENTAL IMPACTS

The environmental impacts of using lead azide occur from its manufacture to its disposal. The wastewater contains heavy metals and extremely low alkalinity, and there are also air emissions and solid waste generation. The environmental impacts arising from the manufacture of lead azide can be observed along all subsystems included in the study, in a greater or lesser extent, involved in the life cycle.

Energetic resource consumption

In the manufacture of lead azide, energy consumption comes from fossil fuels (used by the boiler to generate steam), and especially from electricity, which feeds the agitation, vacuum and product classification equipment, as well as the boiler. In the energy transportation steps, consumption comes from fossil fuel, used only by their respective transportation vehicles.

Atmospheric emissions

The main emissions of the system under study are mainly liquids and solids residues, due to the chemical reaction being a precipitation, taking place in water at temperatures below vaporization point. The majority of atmospheric emissions come from the steam production (CO_2, H_2O, NO_x), which varies depending on the fuel used.

Liquid effluents

For the manufacture of lead azide, excess lead nitrate is used to ensure complete consumption of sodium azide, themost expensive raw material in the manufacturing process. Thus, the mother liquor at the end of the reaction contains excess solubilized lead nitrate and traces of lead azide remaining in solution. This is necessary in the effluent treatment process, in which precipitation can lead to disfigurement and explosion. After addition of these components, a pH adjustment is made and the final effluent is discarded, considering pH and the legal emission limits of 0.01 mg/L for lead (Conama, 2000).

Solid residues

The solid residue is generated only in the effluent treatment step, in which sulphuric acid is later added to the mother liquor for the precipitation of lead sulphate. The recovered lead sulphate is a precipitated solid, which can be treated by co-processing (Curtin *et al.*, 2013; Garg *et al.*, 2013; HasanogĺIu *et al.*, 2012), used in cement or other environmental ways of disposing solid residues.

CONCLUSION

From this study, it can be concluded that the Life Cycle Inventory for a standard lead azide manufactory unit was developed in full, allowing further analysis and a full LCA. Thus, considering the limitations and assumptions made during the study, it is understood that the objectives have been achieved with the desired quality. The raw material considered in this study did not have their manufactory and transportation taken into account. Regarding energy and utilities, this may vary according to the actual facility under study.

Regarding limitations, one of the most important of this study is the allocation and use of lead azide, due to the complexity of use of the explosive after being loaded. Given the wide range of environmental aspects raised in an LCI and LCA, Haddad *et al.* (2013) suggest the application of selection criteria that allow the separation of only the most significant environmental aspects from the total surveyed. From this study, it is possible to summarize the inputs and outputs of the lead azide manufactory process, which were presented in Table 6.

Table 6. Summary of inputs and outputs.

	Inputs	Outputs
Materials	Ethanol 96% GL Sodium azide 99% Sodium citrate Sodium hydroxide 93% Dextrin Lead nitrate 98%	Lead azide Wastewater Lead sulphate
Energy	Electricity	Heat
Utilities	Fuel (petrol based)	CO_2 H_2O NO_x Heat Steam Hot water

Furthermore, this study was successful in filling some of the gaps in the literature regarding the manufacturing of explosives, as well as their life cycle inventory. The environmental impacts were mapped and the process was inventoried, which allows researchers to use this study as background information on lead azide manufactory, as well as its LCI, in future researches.

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