Risks generated by the treatment of aerosol in the recycling of metals : how to secure the process ?

Agnès Janes, Fabrice Malet, V. Herrenschmidt-Munoz

Risks generated by the treatment of aerosol in the recycling of metals: How to secure the process?

A. Janes[1*], F Malet[1] and V. Herrenschmidt-Munoz[2]
[1]INERIS, Accidental Risks Division, Parc ALATA BP2, F-60550 Verneuil en Halatte, France
[2]ECO-EMBALLAGES S.A., 50/52 boulevard Haussmann, F-75009 Paris, France

*Corresponding author: E-mail: agnes.janes@ineris.fr, Tel +33 3 44 55 61 42, Fax: +33 3 44 55 65 65

Abstract
Aerosols consumed at home are supported in France in the recycling of aluminum or steel household waste stream. This process requires storage and crushing in a press, the latter operation leading as indirect consequence in random perforation of aerosols. As aerosols include flammable gaseous, liquid or liquefied chemical compounds, this process can induce fire and explosion hazards. Such incidents have been reported by many waste sorting plants in France.
This work analyses potential of hazard associated to full or empty aerosols recycling. Three types of hazardous scenarios have been identified: 1) an ignition of an explosive atmosphere, 2) a BLEVE occurrence and 3) a liquid pool fire. In each case, the potential effects have been quantified.
Then, technical and organizational solutions are proposed to prevent these fires and explosions and to protect waste sorting plants, regarding hazards associated to the treatment of aerosols.
Keywords: metal waste recycling; aerosols; fire hazard; explosion hazard.

1. OVERVIEW

Products packaged in aerosol propellant form include 1) a liquid base containing the active ingredient dissolved in a flammable solvent or in water and 2) a propelling gas, which is often liquefied petroleum gas (LPG) (iso-butane, butane and/or propane) or dimethyl ether. Some hazardous properties of these substances are listed in tables 1 and 2. Flammable propellant replaced the chloro-fluoro-carbons (CFCs) nonflammable, but that were progressively banned from the market due to their ozone depletion potential in recent past. .

Table 1. Available information on the hazardous properties of most common flammable propelling gases [1] to [5]

	Butane	Iso-butane	Propane	Dimethylether
CAS number	106-97-8	75-28-5	74-98-6	115-10-6
Flash point (°C)	- 73.9	- 82.8	- 104	- 41
Auto-Ignition Temperature (°C)	285	460	450	350
Minimum Ignition Energy (mJ)	0.25	Not available	0.25	0.29/0.45
Flammability Limits (% vol.)	1.8 – 8.4	1.8 – 9.8	2.2 – 10	3.4 – 26.7
Ebullition Temperature at 1 bar (°C)	- 0.5	- 11.8	- 42	- 24.8
Vapour density (air = 1)	2.07	2.0	1.54	8.16
Heat of Combustion (MJ/kg)	45.6	45.3	46.0	28.8

Table 2. Available information on the hazardous properties of most common flammable solvents [1] to [3]

	Iso-pentane	Ethanol	Methanol	Iso-propanol
CAS number	78-78-4	64-17-5	67-56-1	67-63-0
Flash point (°C)	- 56.7	12.8	12	11.7
Auto-Ignition Temperature (°C)	427	363	385	399
Minimum Ignition Energy (mJ)	0.7	Not available	0.215	Not available
Flammability Limits (% vol.)	1.4 – 8.3	3.3 – 19.0	6 – 36.5	2.3 – 12.7
Ebullition Temperature at 1 bar (°C)	27.9	78.5	64.5	82.3
Vapour density (air = 1)	2.5	1.59	1.11	2.1
Heat of Combustion (MJ/kg)	44.9	26.8	20	30.2

Due to fire and explosion risks, aerosols have always been considered as hazardous by safety regulations. Indeed, aerosols are classified as "flammable aerosols" on the basis on the following criteria:

- Fraction of components classified as "flammable", as defined in the CLP regulation [6]: it can be "Flammable Liquids" (if the flash point is less than 93 °C), "Flammable Gases" or "Flammable solids". The composition threshold is 1 %.
- Heat of combustion.
- Tests results: foam flammability test for a foam producing aerosol can, or ignition distance test and enclosed space ignition test for a spray forming aerosol can.

These test methods are described in the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria [7], Part III, sub-sections 31.4, 31.5 and 31.6.

Table 3. Label elements for flammable aerosols [6]

Classification	Category 1	Category 2
GHS Pictograms		
Signal Word	Danger	Warning
Hazard Statement	H222: Extremely flammable aerosol	H223: Flammable aerosol

As they are usually made of steel or aluminum, aerosols can consumed at home are considered in France as household packaging waste. The process requires several operations comprising handling, storage, crushing in a press. This latter operation leading indirectly to perforation of the aerosols cans.

Although they are mixed with other aluminum or steel waste, their quantity in the overall metal waste mix is not negligible. For example, the proportion of aerosols in the aluminum packaging waste is about 20 to 30% of the overall weight. In an aluminum waste ball of 1.5 m^3 compressed at 330 kg/m^3, the estimated number of aerosols is 1600 [8]. Even if it is emptied by the user, an aerosol still contains residual gas or liquid fractions. The estimated residual weight filling rate is about 2% of initial contents of commercially available products [9] and [10]. Moreover, it is not uncommon to find in the waste not emptied aerosols.

It is why the press operation, and more generally the storage and the treatment of waste containing aerosol, generates fire and explosion risks that need appropriate consideration.

2. HAZARD POTENTIAL

Numerous incidents and accidents have occurred on many waste sorting plants in France. Events identified are fires in press, at the output of waste balls, and explosions in press compression chamber. The impact of these events was sometimes significant: pressure effects, fires spreading and other domino effects have been observed, nevertheless no injury was reported.
This work analyses potential of hazard associated to full or empty aerosols under recycling operations. Three potential hazardous situations have been identified: 1) an ignition of an explosive atmosphere, 2) a BLEVE phenomenon and 3) a liquid pool fire. In each case, the potential effects have been quantified.

2.1 Ignition of a vapour/air explosive atmosphere

The volume of an explosive atmosphere is related to the lower flammability limit and the amount of vaporized fuel mixed with air. Table 4 shows that in most cases, the volume of residual propellant gas content in an empty aerosol is enough to constitute a hazardous explosive atmosphere.

Table 4. Calculation of maximal explosive atmosphere volumes according to the nature and amount of fuel

Fuel	LEL (%)	Estimated volume (l) of the explosive atmosphere corresponding to:	
		230 ml of vapour (average volume of an aerosol propellant)	1000 ml of vapour (maximal volume of an aerosol propellant)
Butane	1.8	12.78	55.56
Iso-butane	1.8	12.78	55.56
Propane	2.4	9.58	41.67
Dimethylether	3.4	6.76	29.41
Iso-pentane	1.4	16.43	71.43
Ethanol	3.3	6.97	30.30
Methanol	6.0	3.83	16.67
Iso-propanol	2.3	10.00	43.48

The volume of gas required to obtain a significant effect in case of an ignition is very low. Indeed, the volume affected by thermal effects induced by the ignition of such an explosive atmosphere can be estimated to 10 times the initial explosive atmosphere volume. For example, the ignition of 10 ml of iso-pentane at 1.4 % vol. in the air may produce thermal effects in a more than 1 m radius sphere.
However, the probability that the gas expulsed is mixed with the air to reach the lower flammability limit is not very high. Actually, the flammable gas concentration is inhomogeneous and this is likely to reduce the actual explosive atmosphere volume obtained.
When aerosols are not completely emptied, the explosive atmosphere volume is also considerably influenced by the flammable liquid or liquefied flammable gas flow due to the crushing operation, which vaporizes as a function of its volatility.

2.2 BLEVE

Distances of to which significant effects due to a BLEVE phenomenon may be observed are depending on the weight of product involved. These effects were evaluated for an aerosol propellant containing a few hundred ml of liquefied flammable gas and with a maximum internal pressure resistance of 21 Bar: the fireball generated is about 5 m in diameter and has an overall duration of 1 s. Side effects related to fragments projections can be much larger. This must however be tempered by the fact that, in principle, aerosols crushed in the process essentially contain a small amount of liquid. Indeed, if no liquefied gas is present in addition, the BLEVE phenomenon cannot occur.

2.3 Flammable pool fire

The distances of thermal effects related to a pool fire scenario can be estimated on the basis of the pool surface and some characteristics of the liquid, such as its specific combustion rate and the flame emissivity. These effects are more important in the case of propellants (e.g. butane, propane or iso-butane) than in the case of solvents (e. g. ethanol or methanol).
Indeed, in the case of a 1 m diameter pool, significant burns are reached at about 1 m for solvents and 5 m for the propellants.

3. FIRE AND EXPLOSION RISKS MITIGATION

One of the aims of this study is to identify technical and organizational solutions to prevent these fires and explosions and to protect waste sorting plants, regarding hazards associated to the treatment of aerosols. Some of them have been listed in [9] and [10].

3.1 Prevention of a flammable pool and/or an explosive atmosphere formation

In order to reduce the probability of a fire or an explosion, one workable way consists in controlling the flammable substances overall emission release potential. By contrast, preventing the occurrence of ignition of a flammable atmosphere is not feasible in the crushing process. Indeed, several safety measures can be considered without modifying the sorting plant processes.

Prohibition of not completely emptied aerosols from entering the crush process

- Introduction of control procedures at the most appropriate steps for collecting, receiving and sorting wastes can help the verification that aerosol propellants does not contain residual liquid. Generators containing liquid should not be directed in the press.
- When aerosols contain residual liquid or if they are not empty, a safe drain step is necessary. This could be done manually in an inerted fume hood or eventually in a special automatic device. In both cases, liquid and gaseous effluents must be treated to prevent their release into the environment.

Prevention of the liquids accumulation on the bottom of the press:

- It is recommended to alternate the type of wastes treated in a press, so as to avoid sequences which lead to processing series of balls of metal containing aerosols within a row.
- A retention vat located at the bottom of the press would help to collect the liquid flow and reduce the potential surface of the pool. This vat must be cleaned at regular intervals.

Aspiration and dilution of flammable gases in the press:

- A vapour extraction system can be implemented into press compression chamber. The extraction flow must be adapted to the amount of aerosols contained in the wastes. This extraction system must be shutdown in case of fire detection.

3.2 Mitigation of the detrimental effects of a fire or an explosion

Effects of fires or explosions that could occur must be controlled to ensure the health and safety of workers. The spread of a fire can be avoided by using some safety measures:

- Any combustible material must be kept in a remote position from the press. This includes waste bales waiting for evacuation. The minimum safe distance is estimated to 8 m. Another solution can be the protection by a protection wall made of incombustible material (concrete…) between combustible materials and the press.

- A water injection system is recommended into the press compression chamber and into the press supply column. This water injection could be combined with automatic fire detection and emergency procedure like powering off the crush operation.

3.3 Organizational safety measures

Technical solutions described above must be completed by organizational measures:

- Any intervention in or near the press must be prohibited during the crush operation of aluminum wastes. These hazardous locations around the press must be clearly identified, and marked by visual signs and not reachable (or rendered as normally prohibited areas).
- Finally, operators must be informed about hazards and risks linked to the crushing of metals wastes containing aerosols. They must also be trained to have an appropriate response in case an incident occurs like a fire or an explosion into or near a press.

4. CONCLUSION AND PROSPECTS

Evaluation and mitigation of fire and explosion risks generated by the recycling of metal wastes containing aerosols is particularly important insofar as the amount of waste to be recycled is still increasing.
Moreover, labor regulation entails general requirements from employers that the explosion and fire hazards are assessed and that appropriate measures are taken to ensure worker safety.

References

[1] Modélisation d'un incendie affectant un stockage d'aérosols, Rapport Ω-4, Méthodes pour l'évaluation et la prévention des risques accidentels, INERIS, 2002, http://www.ineris.fr/centredoc/aerosol.pdf

[2] Weiss G., Hazardous Chemicals Data Book, 2nd edition, Noyes Data Corporation, USA, 1985

[3] Medard L., Les explosifs occasionnels, Vol. 1: Propriétés, 2nd edition 1987

[4] INRS, Les mélanges explosifs, Gaz et vapeurs, Ref. ED911, 2004

[5] M. Nifuku et al., An investigation on the static electrification of dimethyl ether, Journal of Electrostatics 64 (2006) 471-476

[6] Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006. OJ L 353, 31.12.2008, p. 1–1355.

[7] UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, ref. ST/SG/AC.10/11/Rev 4, 2003

[8] TERRA. SA Company, Rapports d'analyses de composition d'aluminium issu de collectes sélectives, 2010, personnal communication

[9] Smith D.N., Simmons J.B., Jefferson M.D., Jackson P., Barney M., The use of can flatteners in MRFs for processing material including post consumer aerosols – a risk assessment, Resources, conservation and Recycling 31 (2001) 115-135

[10] Smith D.N., Linton D., Health and safety issues in port-consumer aerosol container recycling, Resources, conservation and Recycling 31 (2001) 253-263