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Evaluation and Mitigation of Fire and Explosion Risks due to the presence of Aerosol Cans in Metal Waste Recycling

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In France, empty household aerosol cans are collected for recycling and separated together with aluminum and steel household wastes. This process requires storage and crushing in a press, the latter operation leading, as unavoidable consequence, to random perforation of aerosol cans. As these 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 the potential hazards associated to full or empty aerosol cans recycling. Three types of hazardous scenarios have been identified: 1) an ignition of an explosive atmosphere (ATEX), 2) a Boiling Liquid Expanded Vapour Explosion (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 mitigate their effects, regarding hazards associated to the treatment of aerosols in waste sorting plants.

Keywords: Metal Waste Recycling; Aerosols; Fire Hazard; Explosion Hazard; Explosive Atmosphere

Overview

Products packaged in aerosol propellant form are principally foams, shaving gels or hygiene, household and automotive products (Kleniewski 2004).

They 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 however 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 (INERIS 2002, Weiss 1985, Medard 1987, INRS 2004, Nifuku et al. 2006).

	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 ⁻¹)	45.6	45.3	46.0	28.8

Table 2. Available information on the hazardous properties of most common flammable solvents (INERIS 2002, Weiss 1985, Medard 1987).

	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

	Iso-pentane	Ethanol	Methanol	Iso-propanol
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 ⁻¹)	44.9	26.8	20	30.2

The alcohol used is, in 80 to 95 % of cases, methyl alcohol, ethyl alcohol or isopropyl alcohol. The active ingredients score usually between 5 and 20 weight % of the liquid contained. The proportion of propellant in an aerosol spray generally varies between 60 and 95 weight %. The solvent and the propellant are usually flammable. However, the solvent may be aqueous. This is the case of shaving foams and gels, which are mostly water-based products containing less than 5% of propellant and so called "alcohol-free" (INERIS 2002a).



Aerosol cans are generally made of steel or aluminum. Their capacity ranges from 150 to 1000 ml. They are normally designed to withstand a maximum internal pressure of 20 bar, which is the value set in regulations.

Due to fire and explosion risks, aerosol cans have always been considered as hazardous by safety regulations. Indeed, aerosol cans are classified as "flammable aerosols" included in hazard category 1 or 2, on the basis on the following criteria:

- Fraction of components classified as "flammable", as defined in the CLP regulation (European Commission 2008): it can be "Flammable Liquids" (if the flash point is less than 93°C), "Flammable Gases" or "Flammable solids". The regulatory composition threshold is set to 1%.
- Heat of combustion.
- Tests results: foam flammability test for a foam producing aerosol can, or ignition distance test and enclosed space ignition test (drum 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 (UNO 2010), Part III, sub-sections 31.4, 31.5 and 31.6. The labeling of flammable aerosols, as defined in CLP Regulation (European Commission 2008) is summarized in Table 3.

Table 3. Label elements for flammable aerosols (European Commission 2008).

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, aerosol cans consumed at home are considered in France as household packaging waste. The treatment process for recycling requires several operations comprising handling, storage and crushing in a press as showed in Figure 1. This latter operation leading indirectly to perforation of the aerosol cans.



Figure 1. View of a crushing press used for aluminum waste recycling.

The waste stream falls from above part of the process into the supply column and is gradually compressed by a horizontal piston. Once produced, the compacted waste bale is ligated with a steel thread.

It seems that the design of the press compression chambers may vary. This could influence the risk of formation of an explosive atmosphere (ATEX) in the press. Indeed, a gas-tight compression chamber promotes the confinement of flammable vapours inside the system. However, a compression chamber enclosed but permeable to gases through mesh side walls can avoid the accumulation of these flammable products. Moreover, the pressure effects will be higher in the case of a gas-tight compression chamber.

Although they are mixed with other aluminum or steel waste, the quantity of aerosol cans 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 bale of 1.5 m³ compressed at 330 kg.m⁻³, the estimated number of aerosol cans is 1600 (TERRA S.A. 2010). Even if it is emptied by the user, an aerosol still contains residual gas or liquid fractions. The estimated residual weight filling ratio is about 2 % of initial contents of commercially available products (Smith et al. 2001, Smith & Linton 2001). Moreover, it is not uncommon to find in the waste feed unused or only partially used (e.g. not emptied) aerosols.

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

A review of pertinent accidents by use of keywords “waste” and “aerosol” was conducted using the French ARIA (analysis, research and information on accidents) database (MEDDE 2013), which is operated and regularly updated since 1992 by the French Ministry in charge of environment. It lists and describes the accidental events which have, or could have damaged health or public safety, agriculture, nature or the environment, in France and to lesser extent abroad. These events are mainly caused by industrial or agricultural facilities. This research returned 24 results from 1994 to 2006, of which 18 were considered as relevant. However, research in this database cannot be seen as exhaustive.

The exploitation of these results reveals a high frequency (15 of 18 cases) of fires involving bulk storage of aerosol, mixed or not with other household or industrial waste. In the last three cases, an explosion was directly caused by the compaction (1 case) or the grinding (2 cases) of waste containing aerosol. In case of fire events, the ignition source is usually unknown (11 cases out of 15). We note, however, two cases of exothermic chemical reactions in industrial waste, one ignition by a hot spot when loading a truck with a bucket and one case of vandalism.

More generally, description of accidents highlights (Descourrières 2005):

- A high frequency of accidents in storage, such as warehouses or retail stores,
- Fires are often linked to the drilling of an aerosol can, and then the ignition of the resulting gas leak,

- The fire spread extremely rapidly, driven by projections of burning aerosol cans,
- Extensive damages are produced,
- These fires are particularly difficult to extinguish.

Potential hazardous scenarios and consequences

Although only a few accidents were recorded in accidents databases, numerous incidents have occurred on many waste sorting plants in France. Events identified are fires in press, at the output of waste bales, 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 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.

Ignition of a vapour/air ATEX

As a first approximation, it can be considered that the level of damage depends principally on the ATEX volume. Specifically, the European ATEX guidance (European Commission 2005) proposes to consider the following two criteria:

- Absolute volume: an ATEX is considered as hazardous if its volume exceeds 10 l,
- Relative volume, compared to the volume of the confinement where the explosion occurs: an ATEX is considered as hazardous if its volume exceeds 1/10 000 of the room volume.

The volume of an ATEX is related to the lower flammability limit (LFL) and the amount of vapourized fuel mixed with air. Table 4 shows that in most cases, the volume of residual propellant gas contained in an empty aerosol is enough to constitute a hazardous ATEX when it is discharged in air.

Results on Table 4 are based on the hypothesis that an empty aerosol still contains its volume of pure propellant gas at atmospheric pressure.

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

Fuel	LEL (Vol. %)	Estimated volume (l) of the explosive atmosphere produced by mixing air with:	
		230 ml of pure vapour (average volume of an aerosol propellant)	1000 ml of pure 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 ATEX can be estimated to 8 to 10 times the initial ATEX volume. The maximal radius of the sphere including thermal effects of most common propellants, as a function of flammable gas volume involved, is represented on Figure 2, while Figure 3 deals with flammable liquid volume.

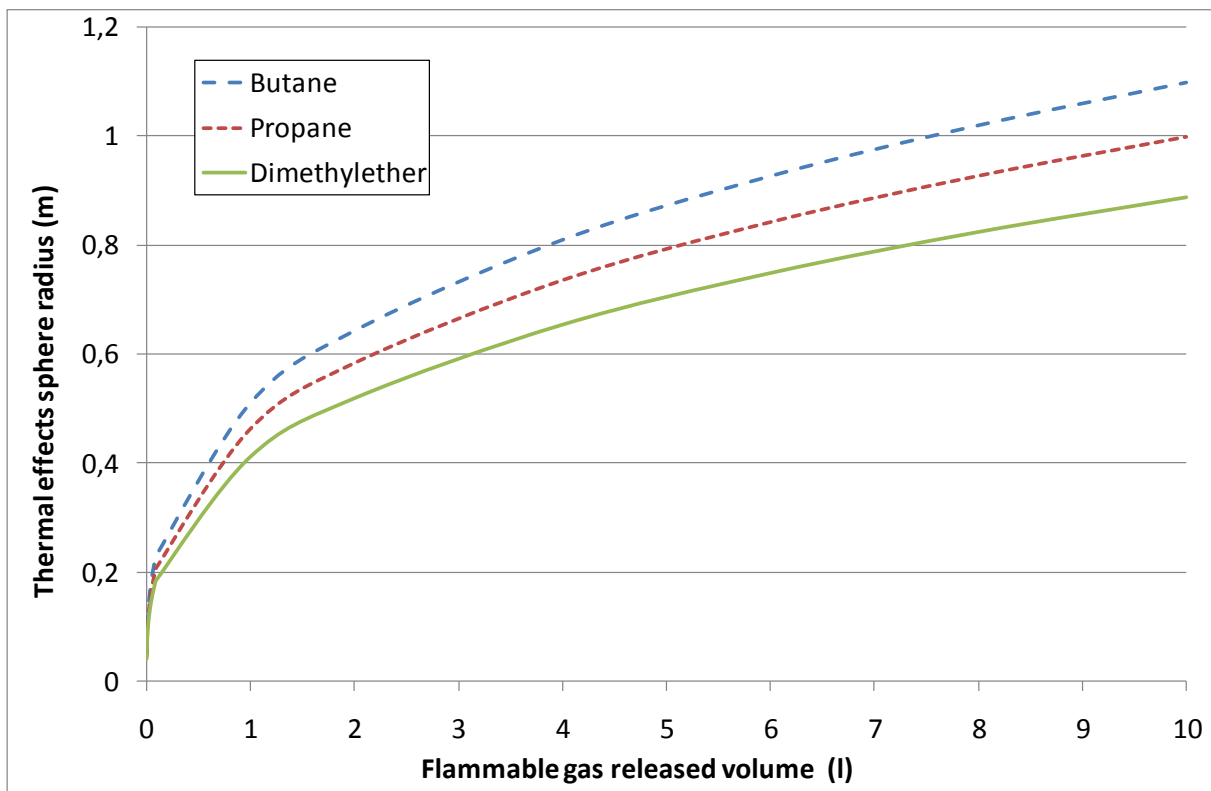


Figure 2. Maximum thermal effects sphere radius obtained during an ATEX explosion, as a function of flammable gas released volume.

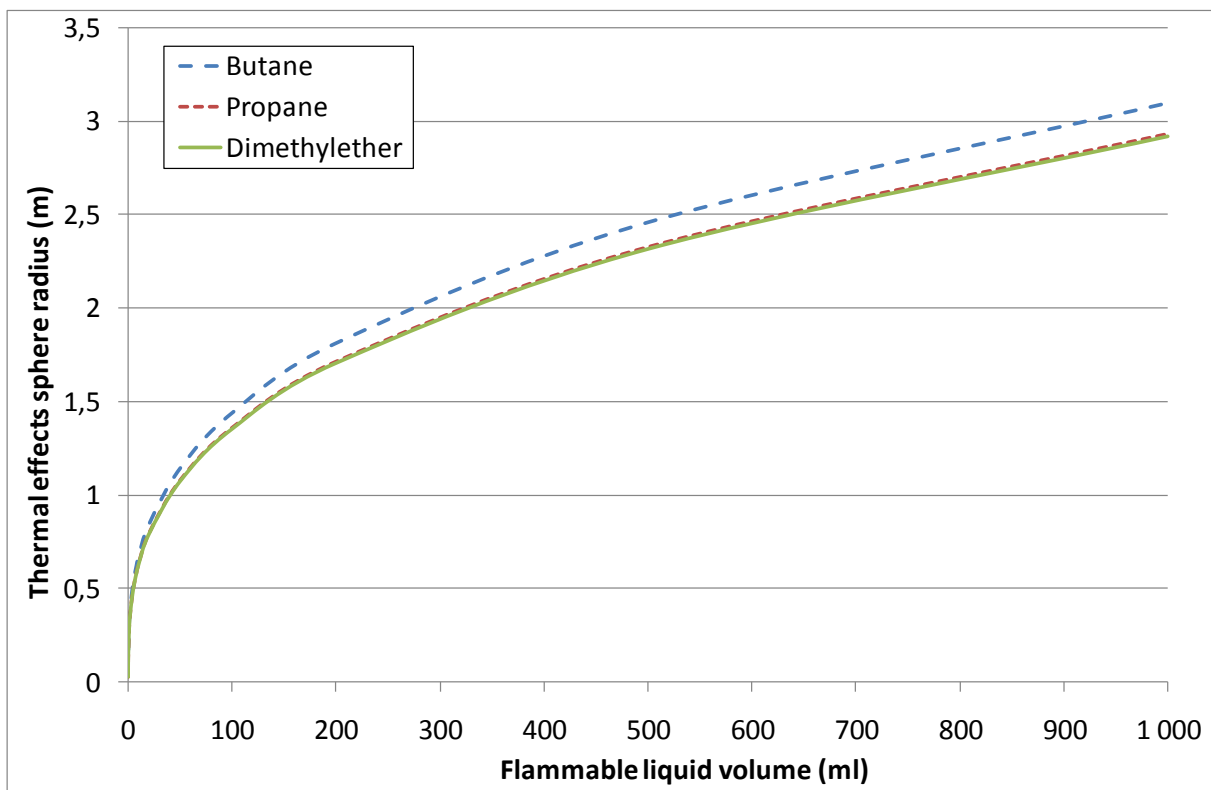


Figure 3. Maximum thermal effects sphere radius obtained during an ATEX explosion, as a function of flammable liquid volume.

For example, as showed on Figure 2, the ignition of 10 ml of gaseous propane diluted at 1.4 vol.% in the air may produce thermal effects in a 10 cm radius sphere. In the case of 10 ml of liquid propane (Figure 3), thermal effect may affect a more than 60 cm radius sphere.

However, the probability that the gas expelled is mixed with the air to reach the lower flammability limit (LFL) is not very high. Actually, the flammable gas concentration is very inhomogeneous and this is likely to reduce the actual ATEX volume obtained.

When aerosol cans are not completely emptied, the ATEX volume is also considerably influenced by the flammable liquid or liquefied flammable gas flow due to the crushing operation, which vapourizes as a function of its volatility.

The minimum ignition energy of flammable liquids or liquefied gas vapours is less than 1 mJ, i.e. extremely low. These vapours can be ignited by all kinds of electrostatic, mechanical or electrical sparks. Their ignition can also occur due to a hot surface, as auto-ignition temperatures of these products varies from 350 °C (dimetyler) to 535 °C (propane).

In the particular case of storage, it is possible to reduce the frequency of occurrence of these various ignition sources.

BLEVE

A BLEVE is an explosion phenomenon of a pressurized tank containing a liquid whose temperature is much higher than its boiling point under atmospheric pressure. The effects of such an explosion are usually the generation of a pressure shock wave, the projection of fragments at sometimes very important distances and finally the combustion in a fireball. This latter effect occurs only if flammable liquid is involved.

Distances to which significant effects due to a Boiling Liquid Expanded Vapour Explosion (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.

Flammable pool fire

The amount of flammable vapours emitted from a liquid is a function of temperature. Propellant gases and flammable solvents contained in the aerosol cans emit enough vapours as to trigger an ignition risk at room temperature. The consequences of a pool fire are mainly related to the thermal radiations, to the smoke generated, either to toxic gases they convey, or to the reduced visibility induced and finally to water or soil pollution by fire-fighting water (INERIS 2002b). Unlike ATEX or BLEVE explosion phenomena, a flammable liquid pool fire is a slow kinetics phenomenon. This allows initiating actions in order to possibly reduce the consequences.

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.

Figure 4 shows the effects of distances corresponding to significant burns, due to a 8 kW/m² thermal flow, to the four most common flammable substances found the aerosol cans, and for circular pools with diameters varying between 0.5 m and 3 m. These effects are more important in the case of propellants (e.g. butane or propane) 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.

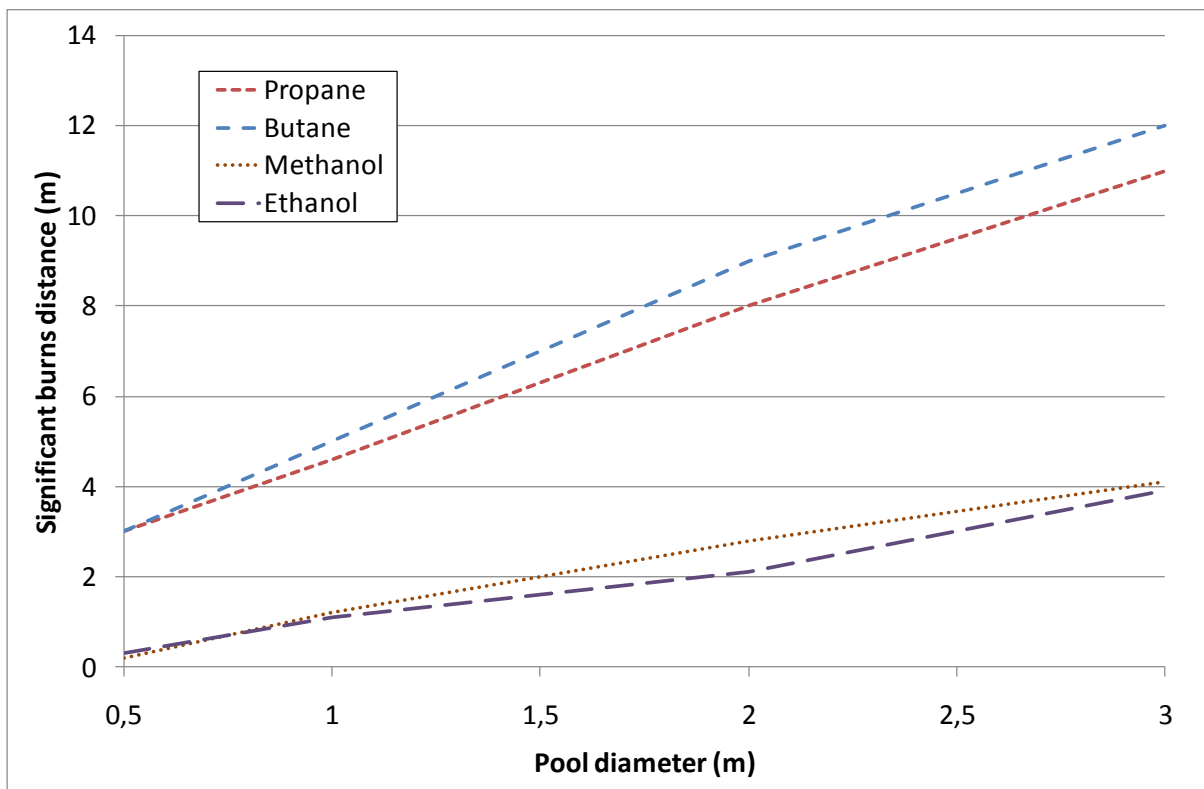


Figure 4. Significant burns distance, as a function of ignited flammable liquid pool diameter.

It must be noticed that, if no residual liquid is present in aerosol cans, a flammable pool cannot be formed during compression.

Fire and Explosion Risks mitigation

One of the aims of this paper 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 aerosol cans. Some of them have previously been listed in (Smith et al. 2001, Smith & Linton 2001).

Prevention of a flammable pool and/or an ATEX 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 an ATEX is not rationally feasible in the crushing process. Indeed, several safety measures can be considered without modifying the sorting plant processes.

- 1) 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 do not contain residual liquid. Aerosol cans containing liquid should not be introduced in the press.
 - When aerosol cans 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.
- 2) Prevention of the accumulation of liquids at the bottom of the press
 - It is recommended to alternate the types of waste treated in a press, so as to avoid sequences which lead to processing series of bales of metal containing aerosol cans within a row.
 - A retention tank located at the bottom of the press would help to collect the liquid flow and reduce the potential surface of the pool. This tank must be cleaned at regular intervals.
- 3) Aspiration and dilution of flammable gases in the press
 - A vapour extraction system can be implemented into the press compression chamber. The extraction flow must be adapted to the amount of aerosol cans contained in the waste. This extraction system must be shutdown in case of fire detection.

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 remotely from the press. This includes waste bales waiting for evacuation. The minimum safe distance is estimated to 8 m. Another solution can be the construction of a fire resistant protective wall (concrete...) between the press and combustible materials.
- 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.

Organizational safety measures

Technical solutions described above must be completed by organizational measures.

Any intervention in or near the press should not be allowed during the crush operation of metal waste containing aerosol cans. These hazardous locations around the press must be clearly identified, marked by visual signs as showed on Figure 5 and not reachable, or rendered as areas where presence of workers is not allowed.

Finally, operators must be informed about hazards and risks linked to the crushing of metal waste containing aerosol cans. They must also be trained to have an appropriate response in case an incident occurs like a fire or an explosion inside or near a press.



Figure 5. European Union regulatory sign signaling an ATEX area (European Commission 1999).

Conclusion

Evaluation and mitigation of fire and explosion risks generated by the recycling of metal wastes containing aerosol cans are particularly important in the perspective of safety management insofar as the amount of waste to be recycled is still now increasing.

Moreover, labor regulation entails general requirements applying to employers that the explosion and fire hazards are assessed and that appropriate measures are taken to ensure worker safety.

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