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TOXIC COMPOUNDS GENERATED BY METALWORKING FLUIDS AND ALUMINUM SLAG LANDFILL AND THEIR EFFECTS ON ENVIRONMENT AND PEOPLE

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Abstract

This paper presents an assessment of the toxic compounds released from metalworking fluids (MWFs) used in aluminum solid waste processing and from aluminum slag landfills, and their impact on environmental quality and human health. The mean concentrations of dust, oil mist, aldehydes, volatile organic compounds (VOCs) released from metalworking fluids were determined in machine shops. The exposure in machine shops was quantitatively dominated by VOCs, whose concentrations varied in the range 0.75 to 3.25 mg/m^3, while the maximum levels of 1.54, 0.583 and 0.208 mg/m^3 was found for dust, oil and aldehydes, respectively. The measurements achieved with aluminum slag showed that, when this waste is deposited in landfills, it becomes hazardous to the environment and people by generating undesirable heat, liquid leachate containing heavy metals, toxic and bad smelling gases such as ammonia, phosphine, hydrogen sulfide or flammable gases such as hydrogen and methane. The methane concentration was about 4 vol.%, whereas hydrogen concentration about 70 vol.%. The concentration of ammonia was about 27 vol.%, whereas phosphine concentrations were less than 1%vol. Hydrogen sulphide was detected only in odour threshold gas, but enough to develop bad odor. Temperature in system after 14 days of investigations reached the value of 63^{o}C. All gases formed within a landfill left it, driven either by differential pressure or by concentration gradients. Gas transport processes also include spontaneous gas exchange over the landfill perimeter. The effects of toxic chemical compounds on environment and people health are discussed.

Key words: aluminum slag landfill, environment effect, metalworking fluid, people health risk, toxic compound

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1. Introduction

In the perspective of the improvement of life quality, bad odor and toxic gases pollution are becoming more and more relevant topics related to environmental quality. In fact, among the variables that could influence the citizens' sense of a healthy environment, bad odor and toxic gases emissions play an important role, as they deeply affect the human life quality and psycho-physical wellness. From this reason, in the last decade the scientific community has been developed an increasing attention towards odor and toxic gases pollution, generally caused by different types of industrial activities, all civil and industrial waste treatment plants, landfills, composting plants etc. (Falkinham, 2003; Jayasekher, 2009; Kampa and Castanas, 2008; Salthammer, 2011; Schuhmacher et al., 2009; Terryn et al., 2017). A large number of workers employed in industry to manufacture metal parts used in the production of auto vehicles, aircraft, machine tools, agricultural machinery and equipment, or in works of metal solid

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waste recycling are exposed to the risk of contamination by toxic compounds released by using of metalworking fluids (MWFs) (Dragan et al., 2014; Park et al., 2005; Passman and Rossmoore, 2002). Due to specific properties such as corrosion resistance, lubricants and coolants, metalworking fluids are widely used in manufacturing processes. These fluids are mixtures based on the oil, detergents, surfactants, lubricants, anti-corrosion agents, and other potentially toxic ingredients for the environment and people (Gordon, 2004, Abrams et al., 2000, Childers, 1994). The use of metalworking fluids can cause adverse health effects through skin contact with contaminated materials, spray, or mist and through inhalation from breathing MWFs mist or aerosol. Exposures to MWFs cause health problems that relate to irritation of eyes, skin, nose, throat, lungs (Cohen and White, 2006; Godderis et al. 2007; Henriks-Eckerman et al., 2007). Other possible diseases that may occur include: dermatitis, acne, asthma, hypersensitivity of the lungs, upper respiratory tract irritation, and a variety of cancer. All these disorders have been associated with exposure to MWFs (Godderis et al., 2007; NOISH 2003, 1998). The severity of health problems is dependent on a variety of factors such as the kind of fluid, the degree and type of contamination, and the level and duration of the exposure (Park et al. 2005; Passman and Rossmoore, 2002; Piacitelli et al., 2001). From another point of view, it is known aluminum metal is produced in 42 countries worldwide, including 13 EU Member States, also including Romania.

Romania is a country that produces and uses large amounts of aluminum, hence about one million tons per year of aluminum wastes are produced. These wastes include aluminum dross and slag that are the residual materials produced during an aluminum melting process. After the recovery of a part of metallic aluminum from dross or slag, the fine residue in most cases is direct land filling and it poses a risk to people and the environment (Das et al., 2007; Dash et al., 2008; Drossel et al., 2003; Gil, 2007; Tsakiridis, 2012). When there is deposited and stored in landfills, slag is hazardous to the environment by generating undesirable heat, liquid leachate with heavy metals, toxic and smelling bad gases such as hydrogen sulfide, phosphine, carbon monoxide, ammonia. These toxic chemicals and gases can be released into the atmosphere. For the recycling of aluminum wastes by environmentally efficient and friendly method to convert these hazardous wastes into value added products and to recover aluminum (AZoM, 2002; Das et al., 2007; Yoshimura et al., 2008) it requires mechanical processing operations such as cutting, crushing, grinding, milling etc. During machining wastes there are also used metalworking fluids to enhance the machining operations. These are a complex mixture of chemicals which can damage over time and can become hazardous.

In research conducted by us to capitalize aluminum scrap in order to recover aluminum and then the resulting slag to be used to obtain the products with added value such as alumina, hydrogen (David and Kopac, 2012, 2013) there were employed mechanical operations such as cutting, crushing, grinding etc.

These mechanical operations have required the use of metalworking fluids. Thus, in mechanical workshops for mechanical processing of aluminum waste the workers were exposed and at a risk of contamination by fluid vapors released. As a consequence of the existence of this risk we thought it would be useful to assess and this risk and this to be added to those resulting from aluminum slag landfill. Of course, this risk could be assessed individually, but we believe that showing this risk together with the result of aluminum slag landfill is much more eloquent evidence in support of a recycling-based management of aluminum wastes. Following this goal, the paper is focused on the necessity to estimate the generation of odors and toxic gases released of metalworking fluids used to machining the aluminum wastes and also from aluminum slag landfill to prevent environmental pollution and the health risk to the people.

2. Materials and method

Exposure measurements to metalworking fluids were carried out in six machine shops during one month. The 6 workshops chosen for the present study were involved in different kinds of machining operations. The most common processes were cutting, grinding and milling of the aluminum scrap and slag. The number of machinists in the workshops varied from 10 to 25 whereas the number of the machines ranged from 5 to 15. All the 10 MWFs observed were water miscible. In four of the six workshops, more than one MWF was used; the number of MWFs per workshop was one to three. One of the semi-synthetic MWFs was designed to be used without any preservatives, and another one did not contain any alkanolamines. Ventilation measures and use of enclosures varied in the workshops, and some of the local exhaust equipment were also used.

Exposure to airborne of the workers was determined by personal sampling in the breathing zone, in the machine area and with stationary sampling by environment. The number of workers with personal air sampling was three to five at each workshop and up to three samples were taken at the same time in each zone. Personal air samples of volatile organic compounds (VOCs), (Henriks-Eckerman et al. 2007) and inhalable dust were collected from the breathing zone of the workers. A total of eight breathing zone samples were taken for each substance. The VOCs were collected by adsorption on Tenax adsorbents and thermal desorption was used to release the VOCs from sorbent mass to determine their concentration. Oil mist was measured from the breathing zone of the workers in the first three workshops and in the remaining three workshops from one stationary site. The total number of samples was 18. The methods for air sampling and analysis (ISO 2004, NOISH, 2003, CEN 2002) are presented in Table 1. To determine the composition of gases released from aluminum slag landfill, the starting materials used in experiments were: Al slag landfill to SC Cepstra Grup SRL Bucharest, Romania; argon and helium gases with a purity of 99.99% purchased from Linde Company., anhydrous calcium chloride, tetrachloromethane, supplied by Aldrich. Chemical composition of Al slag was determined by atomic absorption spectrometry method using an analyzer type Analytic Yena, Nova 300 and this composition is presented in Table 2. The experiments have started after one week after the experimental system was placed into aluminum slag landfill, Fig. 1a, b.

The experimental setup consisted of a column open at bottom and closed at top (55 cm in diameter) having 12 aeration inlets with 2.5 cm diameter, placed 10 cm above bottom to facilitate passive aeration and was inserted into landfill, at about 25-30 cm above landfill bottom. The system was equipped with a vacuum pump and a selective filter containing anhydrous calcium chloride to adsorb the moisture, as is presented in Fig. 1c.

Table 1. Sampling and analysis methods of air samples in six metal processing workshops

The measured substance	*Number of samples*	*Approximate duration of sampling(h)*	*Sampling method/ Collection medium*	*Analysis method*
Breathing zone samples VOCs	18	2	Tenax sorbent tube	Gas-chromatography (ISO 2004) Portable VOC Monitor MiniRAE 2000 PGM 7600
Inhalable dust	18	8	Cellulose acetate filter	Gravimetry(SFS,1976) Beta-Dust Monitor F-701-20
Stationary samples VOCs	18	2	Tenax sorbent tube	Gas-chromatography (ISO 2004) Portable VOC Monitor MiniRAE 2000 PGM 7600
Oil mist	18	8	Glass fibre filter/ceramic filter	Extraction to tetrachloromethane IR (NOISH, 1996)

Table 2. Composition of Al slag determined by atomic absorption method

Component	*Al*	*Cr*	*Fe*	*Ca*	*Si*	*Na*	*K*	*Cu*	*Zn*	*Ni*	*Mg*	*Ti*	*Pb*	*Mg*
Concentration (wt.%)	43.3	0.088	4.32	0.45	10.9	0.8	0.21	1.17	0.9	0.87	1.85	0.27	0.053	0.2

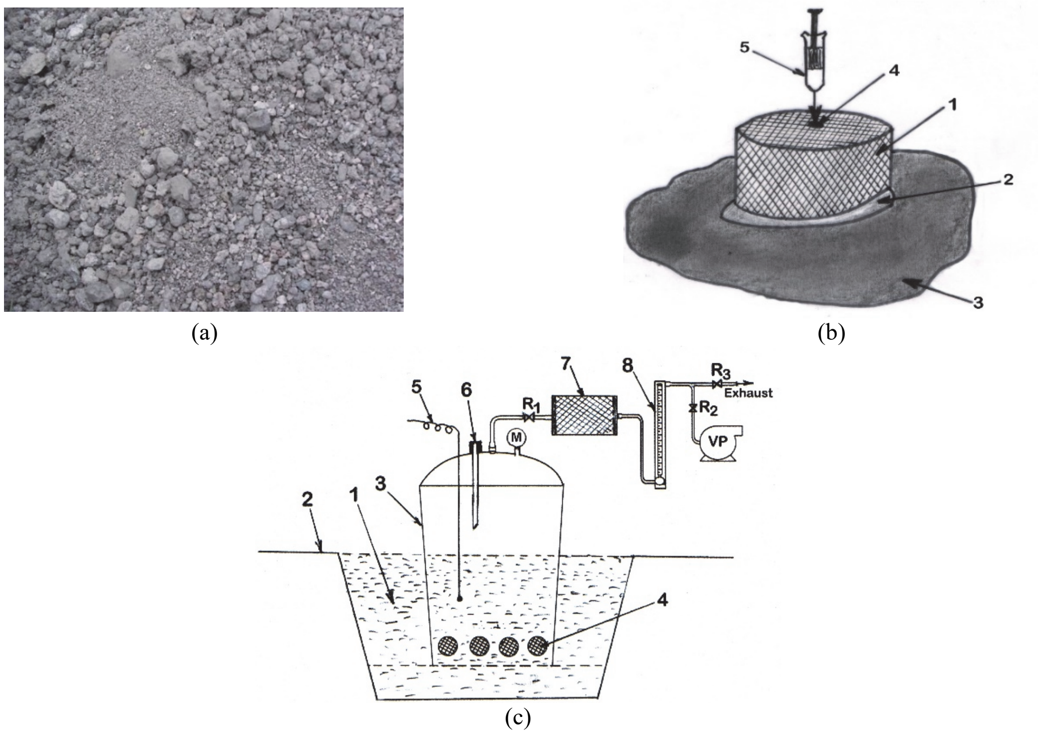


Fig. 1. Emissions measurements: (a) landfill; (b) static system (1- column open at bottom and closed at top; 2-clay sealing; 3-landfill surface; 4-injection port; 5- gas sampling; (c)-schematic representation of the static system used for gas emission measurements: (1)-aluminum slag landfill; (2)-soil surface; (3)-column ;(4)- aeration inlets; (5)-thermcouple; (6)- injection port for sampling gas; (7)- filter; (8)-flow-meter; R_1,R_2,R_3-valves; M-manometer; VP-vacuum pump

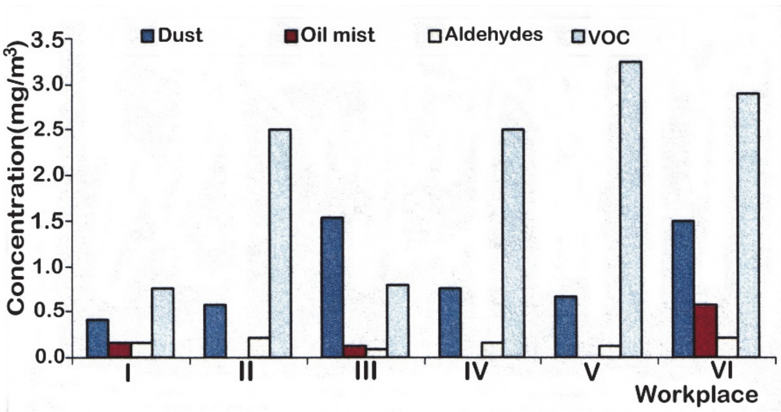
When the system was placed into landfill, valves R_1, R_2, R_3were opened. After the system was placed into landfill, the valve R_3 was closed and the air from system was evacuated for 10 minutes using the vacuum pump (VP) to avoid the forming an explosive mixture of gases during their generation. After this step the valves R_1,R_2 were closed and into the system was collecting the landfill gas generated by aluminum slag. Temperature and pressure in the system were measured by thermocouple (5) and manometer (M). The volume of gas generated was determined by measuring the exhaust gas flow in the system, until the pressure drops to atmospheric pressure. The experiments were conducted during 14 days (including the months September and October of the year) and the samples were collected at different periods of time.

Gas samples were taken using a gas tight syringe (1 ml), to measure gas composition. The concentration of H_2 gas was determined by gas chromatography method using a chromatograph type Hewlett Packard 5890 A, equipped with a packed stainless steel Porapak-Q column and molecular sieve 5A packed column, with a flame ionization and conductivity detectors and argon as carrier gas. For other components helium was used as carrier gas.

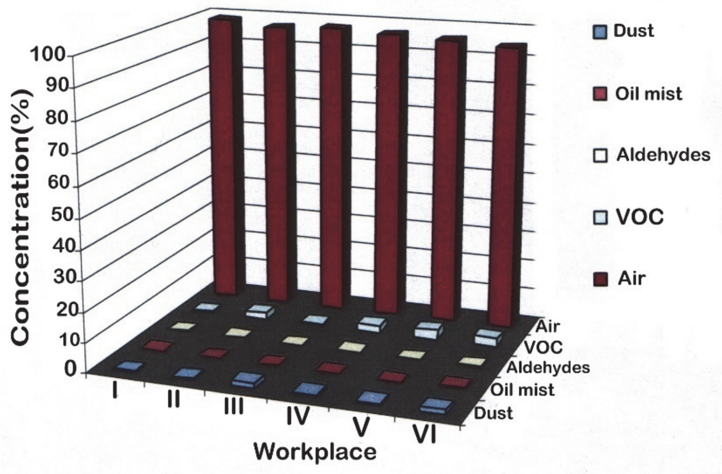
3. Results and discussion

3.1. Odors and compounds released from metalworking fluids use

Water-soluble MWFs are normally used when machining aluminum or aluminum solid waste (Gil 2007). All MWFs are complex chemical mixtures consisting of petroleum oil, vegetable oil or a synthetic lubricating component and various auxiliary substances such as emulsifiers, corrosion inhibitors, extreme pressure agents, antioxidants and preservatives. The chemical and physical nature of the MWFs can lead to contamination of the working environment by oil leakage from machine, by bacteria, the liquid composition that can change over time. The odors released affect people in various ways, especially when they are persistent and powerful, leading to discomfort (Cohen and White, 2006). Odorous substances that are emitted from MWFs include both inorganic and organic gases and particulate. In Table 1 it is presented sampling and analysis methods of air at six aluminum metal workshops. The results have shown that total VOCs formed the main fraction of all airborne impurities for 4 of 6 metal workshops as it is presented in Fig. 2 a, b.



(a)



(b)

Fig. 2. Average air concentrations of dust, oil mist, aldehydes and VOCs in six metal workplaces expressed as: (a) mg/m^3 and (b) vol. percent (%)

The mean concentration of total VOCs was 1.84 (<0.32–4.3) mg/m^3. The main components were different high-boiling hydrocarbons. Aromatic hydrocarbons consisted of, e.g., xylene and toluene, normal hydrocarbons, aldehydes, amines were also identified. The mean concentration of mineral oil mist in six metal workshops was 0.16 (range 0.012–0.63) mg/m^3. All the oil mist concentrations were well below the standard norms (5.0 mg/m^3), and in all machine shops except for one, the oil mist concentrations were >0.2 mg/ m^3, as recommended (Cohen and White 2006). The average concentration of the inhalable dust was 0.74 (<0.12–2.1) mg/m^3, which is small as compared to the norms (Godderis et al., 2007) for both inorganic and organic dust (9 and 4.5mg/m^3, respectively). In two of the six workshops, inhalable dust was the main impurity. The average air concentrations of the assured impurities in each workshop are presented in Fig. 2b.

The average concentration of the inhalable dust exceeded the NIOSH recommended exposure limit for total particulate mass (0.5 mg/m^3). The value is compatible with recently reported concentrations in machining industries (Piacitelli et al., 2001, Abrams et al., 2000). The measurement of inhalable dust is actually a mixture of oil mist and dust, not only the dust. Oil droplets can be retained on the filter.

Only limited information exists regarding the chemical compounds of specific metalworking fluids because of the highly competitive and proprietary nature of the metalworking industry (Childers, 1994; Gordon, 2004). A wide variety of chemicals (i.e. e*thanolamines, mineral oils, antimicrobial agents, chlorinated paraffins)* may be used in each of the metalworking fluid classes, and the risk of these chemicals to workers may vary because of different manufacturing processes, various degrees of refining, recycling, improperly reclaimed chemicals, different degrees of chemical purity, and potential chemical reactions between components. These dangerous components include chemical compounds that are added to metalworking fluids in order to improve certain properties. When using, MWFs can contaminate with germs and bacteria that may occur through the release of formaldehyde. Formaldehyde is an airways irritant and recognized cause of occupational asthma (Falkinham, 2003). Studies suggest that exposure to certain antimicrobial agents can cause allergic or irritant contact dermatitis (Douwes et al., 2003; Henriks-Eckerman et al., 2007). Metalworking fluids may not be safe to use if it will notice any of the following: a change in its appearance; foul smell; floating matter on the surface; excessive foam; dirty machines or trenches; workers with skin irritation; workers with breathing problems.

3.2.Odors and toxic gases generated from aluminum slag landfill

Per ton of aluminum the secondary aluminum industry produces an average of 0.5 ton of slag (Dash et al., 2008; Fukumoto et al., 2000; Tsakiridis, 2012).The slag is a complex conglomerate, including metallic oxides (Al_2O_3, MgO, , FeO, CaO etc.), nitrides (AlN), chlorides ($AlCl_3$, NaCl, KCl), fluorides (CaF_2, NaF, AlF_3, Na_3AlF_6 etc.), carbides (Al_4C_3), sulphides: Al_2S_3), phosphides (AlP), dirt and impurities, apart from metallic aluminium (between 80-20% alumina (Al_2O_3) and rests of metallic aluminum (Das et al., 2007; Fukumoto et al., 2000). So far, most of these slags are stored as special waste in landfills. When they come in contact with rain water or perchlorate can initiate a variety of chemical reactions, most of them are not harmless for the environment.

The waters become concentrated with salts and by hydrolysis of miscellaneous aluminum compounds large amounts of burnable gases are evolved, some of them very toxic. Up to 2.5 million tons/yr salt slag are given to landfills worldwide (Gil, 2007; Sushil and Batra, 2008). About 4.3 million cubic meters waters become saturated with salt and a lot of reactions are initiated. Approximately 40 million cubic meters of gas are released. These gases mainly include hydrogen and methane, but also ammonia, hydrogen sulfide and phosphide. As a consequence they may cause serious problems of environmental pollution. To avoid these negative effects a solution would be recycling aluminum scrap for metal recovery (Das et al., 2007). Fig. 3a demonstrates the gas composition as a function of time for a temperature of 63^{o}C generated from landfill site that has been investigated in this work.

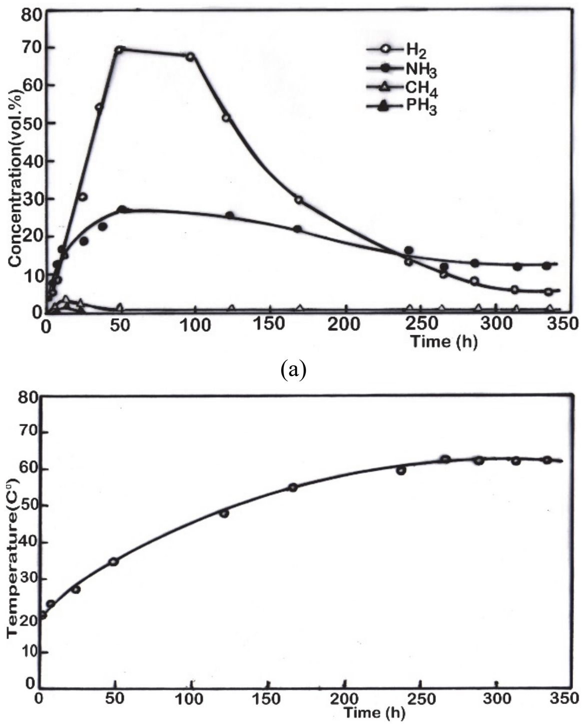


Fig. 3. Gas composition as time function for temperature of 63^{O}C (a) and temperature variation as time function (b)determined in aluminum slag landfill with experimental system presented in Fig.1.

Analyzing this results, it can be seen that the production of phosphine (PH_3) was small (<1%vol) and after half an hour its concentration becomes lower than detectable. Also, the methane concentration slopes down quickly (from about 4%vol till < 1 %vol),whereas hydrogen after an explosion like reaction during the first minutes (about 70 %vol.) come down moderately till about 5%vol. The concentration of ammonia was low at the beginning, due to its large solubility in water remained in landfill and then reached a concentration of about 27 %vol that also come down moderately till about 14%vol. Hydrogen sulphide (H_2S) was detected only in odour threshold gas, but enough to develop bad odor. At first the system temperature was about 20ºC, after 7 and 14 days in system the temperature reached 56ºC to 63ºC respectively.

Fig. 3b shown the evolution of temperature in the experimental system presented in Fig. 1. Hydrolysis reaction at temperature near to ambient temperature leads to a slow degassing reaction, first of all with the evolution of toxic gases that can be completed within a short time. The fast and effective degassing reaction is mainly supported by the hydrolysis reactions, which are exothermic, leading to increased temperature in the system.

The most likely reaction of aluminum production wastes in landfill is the amphoteric reaction of aluminum with water in the presence of hydroxyl ion (Calder and Stark, 2010) (Eq.1).

$$Al_{(metal)}+(OH)^{-1}{}_{aq}+3H_2O_{(liquid)}\rightarrow[Al(OH^{-1})_4]^{-1}{}_{(aq)}+3/2H_{2(gas)}+Heat \quad (1)$$

The main characteristics of aluminum hydrolysis reaction refers to: (i) reaction (1) is interrupted when the amount of aluminum is depleted or when the water is removed from the mass of waste. Both situations are difficult to achieve.

The resulting exothermic events in landfills typically persist for several years; (ii) reaction (1) produces hydrogen gas, with ignition limits between 4 - 75 %(v/v),((Allamagny, 2002); (iii) controlling the reaction and resulting combustion of the surrounding landfill are difficult because exothermic aluminum reactions are usually unrecognized during their early stages, allowing a large amount of uncontrolled thermal energy (approximately 1 mega.J/mol of aluminum) to be released into the waste mass (Drossel et al., 2003). Aluminum slag wastes can remain dormant for years in landfills until enough water enters into waste mass and initiates hydrolysis reactions.

As the dissolution occurs, the pH of the water gradually increases as it reacts with carbides, nitrides, and metal oxides, generating heat and gases, such as methane, ammonia, acetylene and phosphine. As the water in contact with the aluminum waste becomes alkaline (pH≥ 9) hydroxyl ions begin to react with aluminum metal to produce hydrogen gas. The resulting chemical reactions after leachate quality are highly exothermic, increasing water temperature in excess of 100ºC, release large amounts of flammable and/or toxic gases(e.g. ammonia, hydrogen sulphyde, phosphine), cause intense nuisance odors, and reduce desirable anaerobic microbial activity present within a landfill. Elevated ammonia nitrogen concentrations are attributed to the reaction of aluminum nitride with leachate, according to Eq.(2):

$$2AlN+6H_2O_{(liquid)}\rightarrow2Al(OH)_3+2NH_{3(gas)}+Heat \quad (2)$$

Elevated total alkalinity is attributed to the generation of hydroxyl ions from the reactions of leachate with ammonia gas that is very soluble in water (Eq. 3), carbides (Eq.4), basic metal oxides (Eq.5), phosphides (Eq.6):

$$NH_{3(gas)}+H_2O_{(liquid)}\rightarrow NH4^{+}{}_{(aq)}+(OH)^{-1}{}_{(aq)} \quad (3)$$

$$CaC+2H_2O_{(liquid)}\rightarrow C_2H_{2(gas)}+Ca^{2+}{}_{(aq)}+ + 2(OH)^{-1}{}_{(aq)}+Heat \quad (4)$$

$$CaO+H_2O_{(liquid)}\rightarrow Ca^{2+}{}_{(aq)}+2(OH)^{-1}{}_{(aq)} \quad (5)$$

$$AlP+3H_2O_{(liquid)}\rightarrow Al^{3+}+3(OH))^{-1}{}_{(aq)}+PH_3 \quad (6)$$

Gas composition resulting from the hydrolysis reaction change as the process evolves. Appearance of ammonia is the first indicator that signals the release of gas. Water and aluminum nitride are the by-products of the reaction.

The generation of hydrogen associated with aluminum product (Eq. 2) appeared to occur after the generation of the ammonia and methane reactions as the pH of the recycled leachate in contact with the aluminum waste became more alkaline. Other early stage aluminum waste reaction include the generation of methane from aluminum carbide (Eq. 7):

$$Al_4C_3+12H_2O_{(liquid)}\rightarrow4Al(OH)_3+3CH_{4(gas)}+Heat \quad (7)$$

Hydrogen gas generation begins after the oxygen in the waste mass has been consumed and landfill gas may contain till 70% hydrogen by volume (see Fig. 3a).The accumulation of large amounts of hydrogen gas can be a serious problem because hydrogen is extremely flammable, having an explosive range of 4% to 75% by volume in normal atmosphere (Allamagny, 2002). However, hydrogen explosion does not occur since the oxygen level is low in the waste mass, generally less than 3% v / v, much under the amount present in normal atmosphere (20.8% v / v).

With the generation of ammonia, methane, phosphine and hydrogen by aluminum waste reaction, a increase in landfill gas pressure occurred and about 0.5 atm was measured. The aluminum and water reaction also generate considerable heat. Elevated temperatures observed at the case study landfill generally ranged between 20 and 63ºC (see Fig. 3b).In our measurements was not detected gas such as acetylene, although it is likely that this gas also occur, but its concentration may be very low, making it undetectable. The hydrogen sulphide was detected only in odour threshold, concentration being below 5ppm (Allamagny, 2002).

3.3. Effects of odors and toxic gases generated on environment and people health

Exposure to hazardous contaminants in metalworking fluids may present health risks to workers. Among hazardous contaminants provided from metalworking fluids use we determined and analyzed the following compounds:

*Volatile organic compounds (*VOCs). In our measurements the mean concentration of total VOCs was found in the range of (<0.32–4.3) mg/m^3. Respiratory, allergic, or immune effects are associated with VOCs and other indoor or outdoor air pollutants (Piacitelli et al., 2001). Key signs or symptoms associated with exposure to VOCs include conjunctive irritation, nose and throat discomfort, headache, allergic skin reaction, dyspnea, declines in serum cholinesterase levels, nausea, emesis, epistaxis, fatigue, dizziness (Wolkoff et al., 2006).

Formaldehyde. The emissions were found in the range of 0.02 – 0.04 ppm. Respiratory, allergic, or immune effects are associated with formaldehyde emissions. Formaldehyde inhaled may cause headaches, a burning sensation in the throat, and difficulty breathing, as well as triggering or aggravating asthma symptoms (McGwin et al., 2009).

Mineral oil mist. Exposure to mineral oil mist can occur through inhalation, ingestion, and eye or skin contact and this exposure can result in localized irritation of the mucous membranes, and if exposures are excessive, headaches, dizziness, and drowsiness may result (Bernstein et al., 2008,Wang et al., 2007).

Dust particles of different sizes tend to differ in the way they become dangerous (Nowack and Bucheli, 2007,Douwes et al., 2003). The largest particles, like 5-10 microns in size, are deposited in the nasopharyngeal region and may lead to congestion, inflammation, or ulceration. Then, 3-5 micron particles trigger bronchial congestion, bronchospasm, and bronchitis.

We determined an average concentration of the inhalable dust and mineral oil mist that did not exceed the NIOSH recommended exposure limit for total particulate mass (0.5 mg/m^3).

Analyzing the results of our measurements from slag deposits may indicate that these results are important to the management of aluminum solid wastes at landfills and the resulting impact on emissions to the air. Gaseous emissions are also important for the working environment and for people living near landfills and other waste treatment facilities. The main problems associated with gas emissions from this waste are: human health hazards; contribution to greenhouse effect; odor problems; explosion and fire hazards.

The gaseous compounds emitted from these landfills have various impact on their surroundings and act on different scales, as illustrated by Fig. 4.

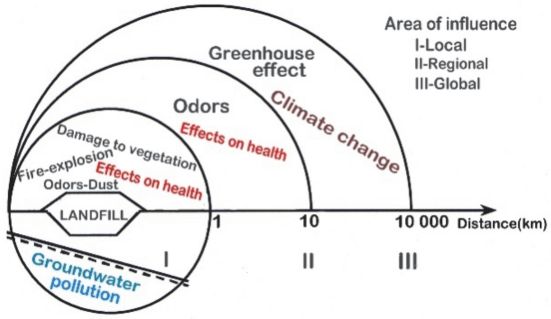


Fig. 4. Different scales of pollutant impact on environment

In addition to having impact over a large spatial scale, gaseous emissions also act on different time scales. Compared to most other processes used in waste treatment, those occurring inside the landfill the emissions which they generate extend over a very long period of time after the waste has been disposed: from tens to hundreds of years. Not only is the period of significant emissions long, but the compounds emitted will themselves have effects and life-spans of varying duration. Methane and hydrogen constitute both a very short term and acute explosion hazard and have a much more far-reaching and long-term effect on global warming. As shown, *hydrogen* is produced in slag deposits. Hydrogen is a non-poisonous, odorless and colorless, but highly inflammable gas. Molecular hydrogen may accumulate during the initial stages and be transiently present at high levels (up to 70%) in the gas phase of landfills, well above its Lower Explosivity Limit of 4%.

Methane was also detected in gas generated from aluminum slag landfill and is an important greenhouse gas. Despite its relatively low atmospheric concentration compared to carbon dioxide (currently 1.75 ppm as opposed to 358 ppm), the higher infrared absorption potential of methane makes its global warming potential some 27 times higher than that of CO2 (Allamagny, 2002). Methane is generally not considered toxic to plants or other organisms. The major effect of methane in soils is believed to be due to methane oxidation which depletes the oxygen present, increases the carbon dioxide levels and may also raise the soil temperature. This may lead to plant death by enhanced asphyxiation due to a lower solubility of gases inside the plant cells or by drying up the soil. The main danger of methane for the people and the environment is due to its flammable and explosive characteristics. Flammability limit of methane in air at atmospheric pressure and room temperature is in the range of 5 to 15%, and the safety concentration in air for closed spaces is 1% (20% of the Lower Explosivity Limit).

Hydrogen sulphide (H_2S) was detected only in odor threshold gas generated from aluminum slag landfill. Humans are extremely sensitive to hydrogen sulfide odors and can smell such odors at concentrations as low as 0.5 to 1 part per billion (ppb), (Allamagny, 2002). Humans can detect the characteristic odor of hydrogen sulfide and is normally described as resembling "a rotten egg". Hydrogen sulphide is highly toxic and affects the nervous system and is highly flammable. Over 50 ppm the hydrogen sulfide paralyzes the olfactory system and it becomes a very dangerous intoxicant. At concentrations bigger than 400 ppm, hydrogen sulfide leads to diseases of the nervous system and above of 700 ppm determines certain risk of death by respiratory failure.

Ammonia (NH_3) was also found in gas composition generated from aluminum slag landfill. NH_3 concentrations up to 100 mg/m^3 are recorded in the literature (Allamagny, 2002) while little data is available for organically bound nitrogen. Its odor threshold is 1 ppm., this very low odor threshold of ammonia can be considered a security factor. The amount of ammonia stripped increases with the pH of the leachate since the $NH_4^+ \leftrightarrow NH_3 + H^+$ equilibrium will be shifted towards NH_3 under alkaline conditions (pH = 9.3), which is the case for leachates from aluminum slag landfills. Ammonia vapors have a sharp, irritating, pungent odor that acts as a warning of potentially dangerous exposure. Odor threshold is 5 ppm, well below the maximum allowed to be a risk of danger or damage. Exposure to high concentrations of ammonia gas can result in lung injury and death.

Phosphine (PH_3) was generated in small concentration of aluminum slag landfill. PH_3 is a colorless, flammable, toxic gas and has a highly unpleasant odor like garlic or rotting fish, due to the presence of substituted phosphine and diphosphine (P_2H_4). Phosphine can be absorbed into the body by inhalation. Phosphine mainly affects the respiratory tract. Exposure to phosphine may occur nausea, pulmonary edema, tiredness. (NOISH 1995). The emissions of *dust and aerosols* on landfill sites cause discomfort for workers, with negative effects on their health.

The gases generated from landfill site have negative impact on environment. All gases formed within a landfill will eventually leave it, driven either by differential pressure or by concentration gradients. Gas transport processes include spontaneous gas exchange over the landfill perimeter. Transport by leachate and storage inside the landfill should also be included in this balance and could be of some relevance, especially for gases with a high solubility in water, such as ammonia as indicated in Fig. 5.

Emissions vary widely over time, both diurnally and seasonally. Several environmental factors may influence both the gas quality and its flux, e.g. changes in barometric pressure, rainfall and temperature. In addition, during the transport of the gas through the soil cover many processes may occur, which will modify the composition of the gas phase, such as the adsorption and oxidation of organic compounds or their solubilization in the liquid phase. Reducing the amount of materials thrown away as waste reduces the amount of new products and, as a result, reduces the contamination of air, water and land. When aluminium wastes are used instead of ore to make aluminum, mining wastes, air and water pollution are reduced. It also reduces the production of hazardous wastes.

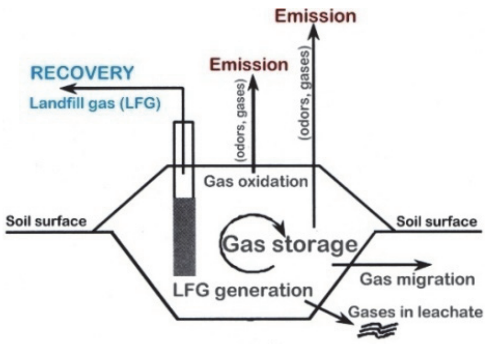


Fig.5. Schematic representation of gas emission process from aluminum slag landfill

Many of the toxic air contaminants released by landfills also eventually fall to the ground becoming surface water contaminants. Other environmental effects include odours, litter, dust, attraction of rats, birds and insects, and aesthetic concerns.For the reasons given,aluminum slag recycling by environment friendly method to convert this hazardous waste into value added products with aluminum metal recovery represents a safe and efficient way to mitigate the bad odor and toxic gases released by storage.

4. Conclusions

The compounds released of metalworking fluids and from aluminum slag landfills undoubtedly determine pollution effects and represent a potential hazard to people health. The total exposure in machine workplace was quantitatively dominated by volatile organic compounds. Maximum concentration was of 3.25 mg/m^3. This concentration was below the standard norms.

Aluminum slag landfills, becomes hazardous to the environment by generating undesirable heat, liquid leachate with heavy metals, toxic and smelling bad gases such as hydrogen sulfide, phosphine, ammonia or flammable gases such as hydrogen and methane. The gaseous compounds act on different scales and have a negative impact on their surroundings.

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