THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^{0}. 2 – 2014, ISSN 1453 – 083X

ASPECTS OF MATERIALS DECAY UNDER CHEMICAL ATTACK FROM THE LEACHATE TREATMENT PLANT OF THE TIRIGHINA WASTE LANDFILL[1]

Doiniţa NEAGU (PÎRVU), Lidia BENEA*, Eliza DĂNĂILĂ
Research (Competences) Centre: Interfaces-Tribocorrosion and Electrochemical Systems (CC-ITES),
Faculty of Materials and Environmental Engineering, “Dunarea de Jos” University of Galati,
47 Domneasca Street, 800008 Galati, Romania
*Corresponding author
e-mail: Lidia.Benea@ugal.ro

ABSTRACT

Human society faces a number of major problems among which the increasingly negative consequences of environmental pollution. The high uses rate of the natural resources and the large amount of waste generated tend to transform the natural environment, its feed back reactions becoming dangerous to both life and the constructive environment created. Waste is one of the best indicators that measure economic vitality and the society way of life. The economic growth and development most times generate a quantitative increase and diversification of the nature of waste produced in the processes of making community utilities. Currently, waste management and treatment have become crucial and complex issues to ensure sustainable development. Because most municipal landfills do not have a perfect waterproof foundation, leachate infiltration into the soil, subsoil and underground water may occur causing the pollution of these environmental factors. To this end the paper is focused on the collection and treatment of leachate from the municipal waste landfill by presenting modern technologies for the collection and treatment of leachate from uncontrolled municipal waste deposits.

KEYWORDS: waste landfill, leachate, corrosion aspects

1. Introduction

Due to harmonization of the national legislation with the European Union one, part of the legislation was adopted. Thus the leachate collection methods presented in the current national legislation refer only to controlled landfills.

There is no standard method for the leachate collection in order to reduce pollution of soil, subsoil and groundwater.

In accordance with the legislation in force, leachate treatment can be performed in two types of systems, namely:

- the treatment plant of the landfill allowing leachate discharge directly into the natural receptor (in this case the Siret river) in compliance with legislation in force;
- leachate pre-treatment plant for disposal in a municipal sewage treatment plant, while complying with the effluent quality parameter values.

In this respect the uncontrolled municipal landfills where there are no collection facilities or leachate treatment plants, a collection and pre-treatment technology can be applied to decrease the concentrations of salts, heavy metals and organic substances.

In uncontrolled deposits/landfills (mostly from Romania) there are no facilities for the collection and treatment of leachate.

The leachate from municipal waste landfill is generally characterized by a high concentration of organic matter and ammonia and contains potentially toxic substances.

In Fig. 1 is shown an overview of the leachate treatment plant from Tirighina waste landfill.

[1] Papers presented at the second edition of the Scientific Conference of Doctoral Schools from “Dunarea de Jos” University of Galati, CSSD-UDJG 2014, Galati, May 15-16, 2014.

Fig. 1. *Overview of the leachate treatment plant*

In some cases, existing organic substances in wastewater are easily degraded by microorganisms; other substances require a selected adapted flora for their removal and other substances are resistant to attack by microorganisms or are degraded in a long time.

A coexistence of organic substances with different capacities of resistance to the action of microorganisms causes difficulties in the biological treatment of wastewater.

In the case of waste water resulting from wastes landfills (leachate) its quality varies with: depositor age, ambient air temperature, the rainfall rate, permeability of waste, waste layer depth, waste temperature, and waste composition.

The basic characteristic of leachate is its variability. Leachate quantity increases during the rainy periods and falls under drough. Concentrations of pollutants from wastes also vary over the life of depositors so that in the early stages leachate is rich in biodegradable organic substances. With increasing depositor's age the leachate is enriched with readily biodegradable complex organic substances.

In addition, changes in leachate characteristics cannot be foreseen from the beginning, therefore no leachate is constant in time and also two leachates will never be the same. To this are added the cost and environmental risk.

The content of ammonia, the odor and the very dark colour are impediments to the introduction of leachate into the municipal treatment plants.

The main methods used to reduce ammonia nitrogen from wastewater are air stripping of ammonia, chlorine intermittent chlorination (break point), ion exchange, biological nitrification.

2. General information on leachate treatment plant from Tirighina waste landfill

In the municipal landfill of Tirighina leachate forms through waste percolation - in various stages of decay – by rain water; precipitation are responsible for producing the largest amount of leachate in the domestic waste landfill, but they are not the only source of percolation agent; a significant amount of water is contained in the domestic wastes and the decomposition of substances also generates significant volumes of water, all of which contribute to the production of additional quantities of leachate.

In the Tirighina waste landfill, leachate will be collected in a built tank of 1000 cubic meters which will accumulate a quantity of leachate produced for about 14 days, where from it is to be pumped to the treatment plant. The treated leachate, also called permeat, will be collected in the rain water retention basin and thence pumped into the Mittal Steel pipline to be further discharged into the Siret river.

The treatment plant is designed to operate a volume of 1400 cubic meters/month, at the rate of 90% availability and 52 cm/day.

Leachate treatment plant includes:

- Ammonia-stripping unit - manufacturer: Devise Engineering AE;
- Reverse osmosis unit - Wehrle Umwelt;
- Building of the chemical storage tanks, pumps and switchboard room and also the spare parts warehouse.

2.1. Description of the leachate pumping station

The pumps draw from the leachate tank and discharge into the leachate tank installed in the container of the ammonia separation plant. A pump will be continuously running and one in stand by.

The pipes inside the plant, as well as the fittings and valves, are made of stainless steel in order to avoid premature corrosion and the discharge pipe from the plant outlet to the inlet of the leachate tank of the ammonia separation unit is made of 63 mm HDPE. For the pipes passing through walls, special parts to maintain tightness have been provided.

2.2. Description of the tanks building

In the leachate plant, of particular importance is the building of chemical tanks. Considering that the leachate plant must operate at temperatures between -20 ºC and + 400 ºC and also at the freezing and boiling temperatures of the chemicals necessary for the leachate treatment technology, it was established the tanks positioning inside a building called the chemical tanks building.

In Fig. 2 is shown the building of chemical tanks which contains the substances used in the treatment of leachate.

For a good operation, the ammonia separation unit requires the following chemicals:

- Caustic soda of 25% concentration causing the pH of the leachate to raise. The caustic soda used in the process (treatment of leachate) is a colorless clear odorless slightly viscous liquid, corrosive to metal materials (depending on the nature of the material metal) and in contact with acids it releases toxic gases.

Fig. 2. *Room tanks with chemical substances*

- Hydrochloric acid at a concentration of 38% with the aim of reducing the leachate pH at the plant outlet. The hydrochloric acid used is characterized as a pale yellow liquid of specific odor, corrosive to metallic materials and in contact with alkanes exothermic reactions occur.

- Sulphurous acid in a concentration of 96% is used in the absorption column. The sulphurous acid mentioned above is a colorless liquid, has a characteristic odor and is a very active mineral acid (not an organic acid); also it is the most important compound of sulfur and the most used in industry, also being called "the blood of the industry".

- Secondary product - ammonium sulphate, which is present in liquid form, is colorless and odorless, non-toxic and non-corrosive.

In Fig. 3 is shown the tank which contains the caustic soda of 25% concentration. It is well known that this solution represent a corrosive environment.

Fig. 3. *Tanks with caustic soda solution*

In Fig. 4 is shown the tank which contains the hydrochloric acid at a concentration of 38% and which also is a highly corrosive solution.

Fig. 4. *Tanks with hydrochloric acid solution*

In Fig. 5 is shown the tank which contains the sulphuric acid solution with a high concentration of 96%.

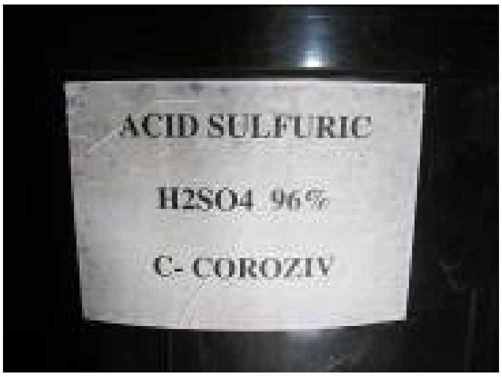


Fig. 5. *Tanks with sulphuric acid solution*

In Fig. 6 is shown the tank which contains the ammonium sulphate solution, which is a secondary product used in the treatment of leachate.

Fig. 6. *Tanks with ammonium sulphate resulting from the process*

***Table 1.** Technical characteristics of caustic soda and hydrochloric acid tanks*

Reservoir	Vertical cylindrical, double-walled
The outer diameter of the double wall	2200 mm
The diameter of the storage tank	2000 mm
The height of the storage tank	3000 mm
The diameter inspection cover	600 mm
Leak detector placed between walls	Provided
Building material	GRP*

**Plastics (P) of glass fiber reinforced resin (GR) is a compound of at least two different materials*

The tank characteristics which contain the caustic soda solution and the hydrochloric acid are shown in Table 1.

The tank characteristics which contain the sulphurous acid solution and the ammonium sulphate solution are shown in Table 2.

***Table 2.** Technical characteristics of reservoirs with a sulphuric acid and ammonium sulphate*

Reservoir	Retention tank leakage
The outer diameter of the vat	1230 mm
The diameter of the storage tank	1140 mm
The height of the storage tank	1170 mm
The diameter inspection cover	360 mm
Leak detector placed between walls	Provided
Building material	PE*

**Polyethylene (abbreviated PE) or polymethylene is a semi-crystalline thermoplastic polymer of white or semi-transparent colour, the most common plastic produced by the polymerization process; it has excellent chemical resistance to acids, bases and oxides.*

Technical characteristics of hydrochloric acid and caustic soda containers:

- cylindrical shape, double-walled;
- construction material: GRP.

The pipes and fittings are made of PE and PVC; containers are made of glass fiber reinforced pastic.

The hydrochloric acid tank (HCL 38%) has the outer cuvette made of polypropylene and glass fiber. The container and the cuvette are made by polypropylene plates soldering. The resistance of the material is adapted to resist to hydrochloric acid at a concentration of 38% and a maximum operating temperature of 40 ºC. Outside both the tank and cuvette there is PAFS reinforced (fiberglass reinforced polyester) which provides high mechanical strength.

The NaOH (25%) tank is a double-walled tank from GRP materials and inner protection PP.

The building where chemicals are stored is a metal construction, closed with heat insulation panels, fitted with electric heating, ventilation, lighting. The heat insulated panels allow for easy dismantling and removal of the tanks, if applicable.

The metallic surfaces are corrosion protected with epoxy.

With the leachate treatment plant at the Tirighina wastes landfill, due to chlorine acid vapours escape and the sulphuric acid itself, undesired reactions took place in the chemical room, monitored over time. The development of the metallic materials corrosion in the chemical tanks building was monitored at different time intervals.

From the thermodynamic point of view, the metal materials in the presence of acid solutions (in this case vapour produces systems which tend to stabilize by the formation of oxides and salts, respectively.

In the following we will pursue some places where it seems that corrosion had a somewhat higher rate.

Corrosion in this case can be regarded as an attack "intensely localized in cracks, crevices or places where the metal material was not properly covered with anticorrosive material or the treatment was not conducted at the prescribed parameters.

3. Corrosion aspect of plants and equipment

First, corrosion was monitored in the chemical tanks building on 17/10/2013.

The most common and known case of chemical corrosion is the "phenomenon of rusting" of the surfaces of iron, cast iron and mild steel; we can say that in this case the chemical corrosion is present as the vapour substances acted on the metallic materials.

At a first examination it seems a pitting corrosion, a form of localized corrosion in which metal is destroyed very quickly in certain discrete points of the surface, the remaining area being quite significantly attacked. This involves the formation of small holes of significant depths. The consequence of such an attack can be rapid and unexpected destruction of the structures on which it occurs. The pitting is more misleading as it occurs on passive materials, which present an excellent resistance to generalized corrosion. A pitting corrosion occurs whenever a metallic material whose coating, no matter what kind, is damaged locally and comes into contact with aggressive solutions (in this case high concentrations of acids, strong acids). Pitting cannot be characterized by indicating the average corrosion rate only but by the circumstances in which localized attack occurs (in this case the acid vapour concentration). The main feature of pitting potential in this case is that metallic materials present in an aggressive environment (presence of acid vapour) get repassivated under pitting potential, and only when this potential is exceeded pitting occurs (as shown in images below).

Pitting is a complex process which takes place in several steps on the surface of metallic materials, namely:

1. destruction of the protective layer;
2. pitting initiation and formation;
3. pitting development.

The phenomenon depends on the nature of the metal or the alloy composition, the characteristics of the environment. Metallic inclusions play a decisive role in the initiation of pitting, but aggressive ions also cause pitting initiation.

The pitting growth rate depends on the composition of the material, the concentration of the electrolyte inside the pit and the potential inside pitting.

In the case of sulphuric acid the following reaction occurs:

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2 \uparrow$$

In the case of hydrocloric acid the following reaction occurs:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2 \uparrow$$

As mentioned above it is a pitting corrosion (oxidation) or the so-called point rust because of the chemicals attack (sulphuric acid, hydrochloric acid). Pitting corrosion is a localized form of corrosion that is active on metal surface on microscopic scale, while being difficult to predict and locate.

Following the reactions between metal and aggressive environment (in this case - chemicals) corrosion products on the metal surface corrosion products, also called film corrosion, still remain. The thickness of the corrosion film largely depends on the environmental temperature, process duration and aggressiveness of the corrosive environments (in this case, hydrochloric acid has very high concentrations – 96%).

Because ventilation does not work at the appropriate parameters and the ventilation ducts of the acid tanks do not run over the roof of the building to the parameters listed in the documentation, corrosion grows in time. As it can be seen, there is a so-called common general corrosion which has the effect of reducing the thickness of the metal over the entire surface or larger portions and varies depending on the material.

A pitting corrosion occurs whenever metallic material whose coating, no matter what kind, is locally damaged in contact with aggressive solutions.

In Fig.7 are shown some aspects of corrosion during the initial phase (a), (c), (e) and (g) caught on 17/10/2013 and in the final phase (b), (d), (f) and (h), on 04/03/2014. Corrosion is found on components of chemical tanks (a - b), on the parts of the support pillars (c – d), on the supporting beams circuits (e – f) and also on the body chemical feed pump (g - h).

Chemicals under the form of vapour, present in the reservoir chamber, attacked the iron (the predominant material the interior of the building is made of) to give reddish-brown oxide that does not stick (as shown in Fig. 7a-f - at metal parts above the chemical tanks), these layers are porous, allow for further oxidation of the metal and fall off. As known from various experiments, in some cases, as a result of the reaction between the metal and an aggressive environment it tends to crumble and fall, revealing the metal surface with which the air and moisture are to react again, thus resulting in loss of metallic properties.

From further monitoring the corrosion activity in the building of chemical tanks, it was found increased corrosion. During the interval for monitoring corrosion, all forms of corrosion could be seen as follows:

a) General surface corrosion - occurs when the metal surface is corroded evenly, unevenly or in patches by acidic and oxidizing solutions. In this case, on the surface of the metallic material, a dark color film is formed from compounds of cohesion (basic salts, carbonates, etc.).

b) Pitting corrosion (pinching - pitting) occurs when the chemical agent attacks the surface points (present in all phases of monitoring), while progressing the phenomenon causes deep holes and even perforation of the metal. It is difficult to assess by the number of points per unit area or by their depth.

c) Intercrystalline corrosion occurs when the attack occurs on crystalline grain boundaries, resulting in structural damage down to the disintegration of the metal, which is also present in this case.

d) Selective or internal corrosion occurs where a metal or an alloy constituent is attacked and destroyed.

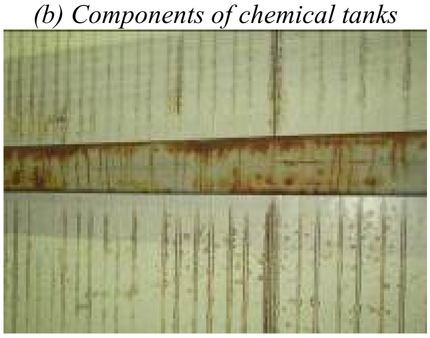
Decomposition of solid solutions is often observed along with separation and attacking only of one component of the alloy, noticed on the water battery which was completely corroded.

Starting with 23/10/2013 we can speak of the notion of thickness of the corrosion films that depend heavily on the process duration and aggressiveness of the corrosive environment.

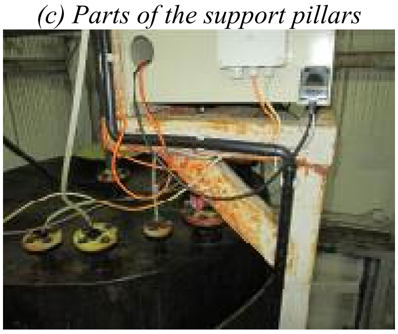
(a) Components of chemical tanks

(b) Components of chemical tanks

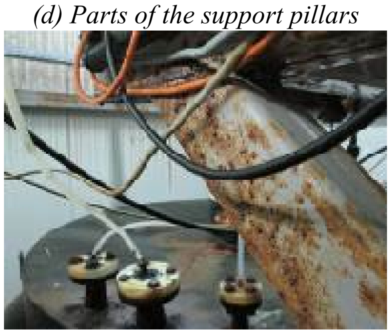
(c) Parts of the support pillars



(d) Parts of the support pillars



(e) The supporting beam circuit



(f) The supporting beams circuit

(g) Body chemical feed pump

(h) Body chemical feed pump

Fig. 7. *Corrosion aspects*

As it is apparent, the film thickness varies within very wide limits, in stages, so one can make some classification according to it, namely:

- thin films are the invisible ones of somewhat smaller thicknesses and can be seen in the initial phase; in this case the specific colour of the metal is affected at times;
- average film thickness which is better highlighted and visible due to the interference of light and appears in slightly different colours (the phenomenon is seen in the period immediately following the initial phase) and then films turn into thick ones and also their colour is very differentiated from that of the metal.

In the case reported, the metal items exposed to the corrosive action, after installation, are no longer accessible (some of them), and not protected against corrosion, during the life of the building they will not affect its durability, but from its monitoring carried out it was found that the entire metal building was subjected to a corrosion process which would result in its destruction in time

4. Conclusion

Immediate action should be taken, for example, the realization of a fan to provide proper air ventilation of the room air thus removing the undesirable chemical or metal vapours.

Currently, methods of stagnating the corrosion process are taken into account due to the presence of high concentrations of chemical substances in this room.

As to metallic materials present in this room they apparently were not treated properly, as protection methods were not met depending on:

- technological parameters of the installation;
- the shape and size of the object to be protected;
- quality of support material;
- protected object location specific to the plant operating conditions;
- application technologies and the possibility of executing the corrosion protection.

Another measure would be anticorrosion coatings which are realized by coating the metal with a thin layer of self protecting material.

The self protecting layer has to meet the following requirements:

- to be compact and adherent;
- to be sufficiently elastic and plastic;
- its thickness to be as even as possible.

Non-metallic coatings can be organic or inorganic, obtained from varnishes, paints, enamels or plastic films, etc.

Acknowledgements

This work was financially supported by the Financing Contract *POSDRU/159/1.5/S/13896 - „Performanță sustenabilă în cercetarea doctorală și postdoctorală – PERFORM",* and partially by research project C2-02/(2012-2015) and Bilateral research project RO-FR, ANCS – Capacitati 702/30-04-2013.

References

[1]. * -** *Technical documentation of the operating system inside Tirighina waste landfill*, Galati, November 2011.
[2]. * -** *Operating handbook on collection and treatment of leachate*, Galati, November 2011.
[3]. * -** *Environmental protection legislation - GD 162/2002 - "The regulation of this activity aims to prevent or reduce as far as possible the negative effects on the environment, in particular pollution of surface waters, groundwater, soil, air, including greenhouse effect as well as any risk to the population health, during the entire life of the waste landfill and after its expiry date".*