Solvents removal from solid waste: an experimental investigation on the mechanisms and supporting conditions

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Abstract

This study is inspired by a concrete industrial problem concerning the disposal of industrial solid waste (ISW) contaminated by flammable solvents. The purpose is understanding factors that facilitate the removal of solvents from porous solids, because the solvent removal is expected to reduce the flammability hazard. This experimental study is based on simultaneous weight, temperature and emission measurements, spanning a large range of sample sizes: both small and large samples are investigated, in order to identify the limiting factors. Three variables were correlated to measure the hazard of the contaminated waste: loss of solvent, Flash Point (FP) measurement and Volatile Organic Compounds (VOC) emissions. While the FP is a discontinuous, off-line measure, the measurement of VOCs and the weight loss are continuous and their correlation provides a real time indication about the residual hazard of the waste during the industrial treatment. The effect of the reaction temperature, the ambient pressure, the sample size, the stirring of solids and their aeration were investigated. We conclude that: the evaporation rate increases as the temperature increases and the pressure decreases; proper aeration achieved by a forced gas flow or a bed stirring, significantly speeds up the solvent release; an increase in sample size increases the diffusion length in the bed, limiting the evaporation rate.

Keywords: Flash Point, Industrial Solid Waste (ISW), Solvent, TGA, VOCs, Weight loss

1. Introduction

With the rapid development of economy and society, environmental problems caused by solid waste pollution, that affect human health and damage ecological security [1] are beginning to appear. Environmental management of the solid waste as an indispensable part of pollution prevention is inseparable from the prevention and control of atmospheric, water and soil pollution [2]. The large quantity of industrial waste poses a huge threat to the environment. Industrial solid waste (ISW) is discharged during specific industrial processes: the storage of ISW not only takes up valuable land resources, but also caused serious environment pollution [3] and dangerous events of uncontrolled fires ([4], [5]). The studies on this topic in general stop at the qualitative analysis of the problem and that makes it difficult to perform relevant decisions [6].

This paper studies the waste management issues pertaining to ISW contaminated with solvents: this topic is complex in nature because the real waste contains a wide variety of chemicals, used during specific industrial processes, which makes it difficult to define and apply a general treatment. For this reason, the analysis of the state of the art showed a gap on this topic in the literature: thus, very few are referenced in the scientific bibliography in which the solvents removal from industrial solid waste is studied, with the aim of making the treated waste disposal safer ([7], [8]). Removal of organic solvents from porous materials has been studied with regards to the solvent recovery and regeneration of porous carbonaceous solids and other adsorbents ([9], [10]). Another field that deals with the removal of an absorbed solvent from a porous matrix is the drying of solids, mainly applied to biological materials ([11], [12], [13]). In our case study, the lack of a requirement concerning the solid matrix integrity, suggests the viability of thermal treatments, which are only limited by the flammability of the solvents being evaporated. The advantage of conventional thermal treatments is the relative low cost and the fact that they can be carried out in equipment with simple technology. The use of vacuum can also be considered, provided the degree of vacuum is not high enough to have an economic impact on the process. The aim of this paper is to evaluate the weight loss profiles of solvent contaminated ISW samples during the thermal and/or vacuum treatment process, by carrying out experiments in self-designed systems. These apparatuses allow evaluating the weight variations during the treatment of the material, varying the operative conditions. Firstly, some tests are performed in a system for small masses; then, a second type of system is used, with apparatuses for larger masses, to evaluate macroscopic effects. This aspect is particularly important when dealing with heterogeneous waste samples, such as those coming from industrial realities. Instead, in the macro TGA used in this study, the effects on the internal (in the material) and external (in the bed) mass transfer (MT) limitations on the solvent extraction rate are investigated, integrating the heat and mass transfer effect. We implement a procedure that allows correlating a continuous measurement like that of the VOCs signal, to discontinuous measurements, like the weight loss and the FP of the waste, obtaining a real time indication about the residual hazard of the waste during the treatment.

2. Materials and Methods

2.1. The solvent contaminated solid waste

The ISW considered in this study, named S-CR1, is a very heterogeneous organic material, as shown in Table 1. All the results of the analyses carried out are reported in Table 1. The weight loss measurements at 105°C are in agreement with the quantitative analyses on solvents, reported in Table 2. All the measurements are carried out using gas chromatography techniques associated with mass spectroscopy.

Table 1: Images and characterization of sample S-CR1

Parameters	**Units**	**S-CR1**	**Quantitative Limit**
Appearance			
Physical state	-	Non-powdery solid	
Color	-	Grey	
Odor	-	Perceptible	
pH	-	6.43	
Water Content	%	21.8	0.1
SS at 105 °C	%	77.6	0.5
SS at 600°C	%	26.6	0.5

The whole presence of PAH and organic aromatic, aliphatic and chlorinated solvents was detected for a total amount of 21190.34 mg/kg (2.12%); instead, the total amount of solvents with a boiling point below 105°C alone (see the IV column of Table 2) adds up to 0.5%: the mass balance on solvents with an evaporation point below 105°C closes with an error of 0.1%, probably due to the presence of trace solvents not detectable by the instrument.

Table 2: Characterization of the solvents in contaminated solid waste

Solvent	**Value (mg/kg)**	**Quantitative Limit**	**Boiling Point (BP) (°C)**
Polycyclic Aromatic Hydrocarbons (PAH)			
Acenaphthene	0.21	0.1	279.0
Phenanthrene	0.18	0.1	336.0
Fluorene	2.8	0.1	295.0
Naphthalene	8.2	0.1	218.0
Organic Aromatic, Aliphatic and Chlorinated			
Acetone	1580	10	56.2
Ethyl Acetate	896	10	77.0
Isobutanol	511	10	108.0
1,2-Dichloropropane	17	10	95.5
1-Methoxy-2-Propanol	1620	10	120.0
2-Butoxyethanol	734	10	171.0
Cyclohexanone	355	10	155.6
Diacetone Alcohol	90	10	166.0
Dichloromethane	152	10	39.6
Ethanol	208	10	78.4
Ethylbenzene	529	2	136.0
Isobutyl Acetate	824	10	118.0
Isopropanol	225	10	82.5
Methanol	722	10	64.7
Methyl Isobutyl Ketone	937	10	116.0
N,N-Dimethylformamide	287	10	153.0
n-Butanol	1700	10	117.7
n-Butylacetate	6520	10	126.0
n-Propanol	51	10	97.0
n-Propyl Acetate	18	10	102.0
Pyridine	160	10	115.0
Ter-Butanol	27	10	83.0
Toluene	603	2	110.6
Tetrahydrofuran	63	10	66.0
Xylenes	2340	2	140.0
Cumene	10	10	152.4

2.2. Experimental procedure

2.2.1. Flash Point Analyser (FPA)

There is not a standard procedure to measure the FP of a solid soaked with flammable solvents. The UE defines the standard methods to measure FP in the council regulation (CE) No 440/2008 [14], but just for liquid substances. We decided to adopt the small-scale equipment SETA flash (STANHOPE SETA Flash 33250-2): a schematic picture of the apparatus is visible in Figure 1.

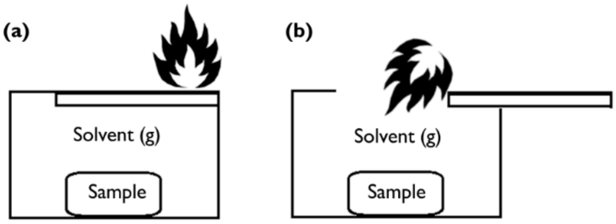

Figure 1: Flash point tester. (a): closed; (b): open

2.2.2. Experimental setup for small masses

Some experiments were carried out in a custom system for small masses. This equipment allows to evaluate the weight variations (i.e. conversion) during the heating of the material, varying the heating rate T(t), pressure (from vacuum to atmospheric pressure) and possibly also the composition of the gases that lap the material. Desorbed VOCs were measured. This apparatus is schematized in Figure 2.

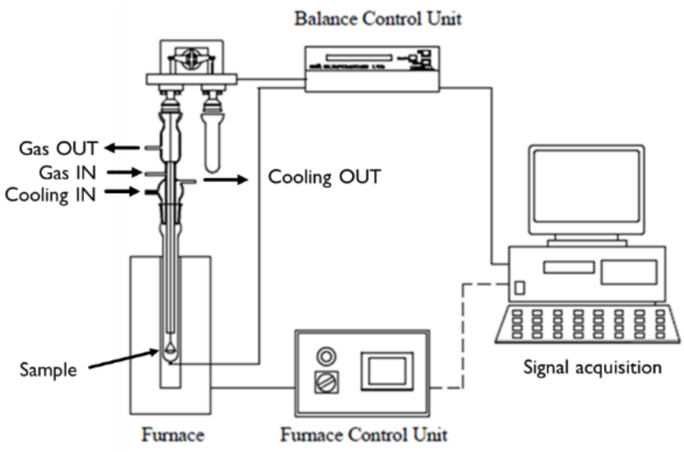

Figure 2: Setup for small masses in standard TGA

2.2.3. Experimental setups for big masses

Experiments with larger mass samples were conducted to evaluate macroscopic effects. A first experiment was conducted in an open vessel, at ambient conditions, to evaluate the natural desorption of solvents. Here, solvents were channelled in a hood, which was covering the sample holder. The desorbed gases were withdrawn through a membrane pump and sent to a VOC sensor, continuously. Mass and FP were evaluated discontinuously, with a sample time of 30 min. This setup is schematically visible in Figure 3.

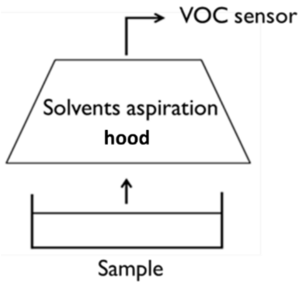

Figure 3: Open vessel setup, at ambient conditions (setup #1)

The second setup (Figure 4) consists of a cylindrical vessel, containing the sample. This was put on a scale, continuously measuring sample weight. The sample was heated by an IR lamp, controlled by two thermocouples, in order to maintain a roughly constant and homogeneous temperature. VOCs were measured continuously.

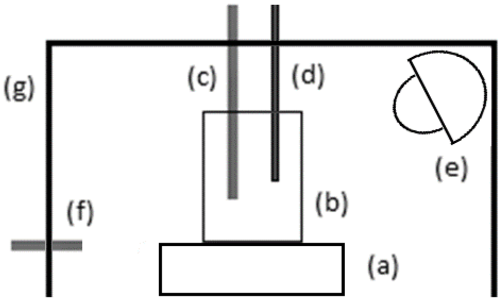

Figure 4: Setup for big mass heated experiments. (a): scale; (b): sample vessel; (c): sample thermocouple; (d): VOCs suction point; (e): heating lamp; (f): chamber thermocouple; (g): PP chamber wall (setup #2)

This last setup was improved by adding a stirrer inside the vessel, to evaluate the effect of stirring on the bed mass transfer (setup #3). An axial impeller was used, with 2 blades, diameter of 6.2 cm. Vessel diameter is 7.6 cm. Here, the weight was measured discontinuously to avoid interference by the impeller, which was stopped to conduct each measurement.

The last implemented experimental setup is an aerated bed (Figure 5), to evaluate the effect of aeration on the mass transfer through the particles. This was realized by putting a diffuser in the same vessel of the previous setup. A layer of gravel was put over the diffuser, to better disperse the air flux coming from the diffuser and to generate a more homogenous field of motion. The samples were put over this layer of gravel.

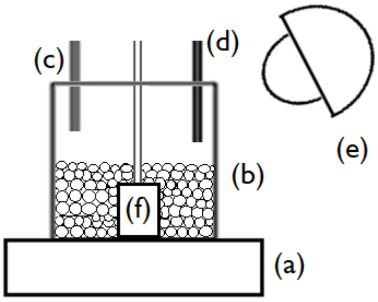

Figure 5: Aerated bed setup. (a): balance; (b): sample vessel; (c): sample thermocouple; (d): VOCs suction point; (e): heating lamp; (f): diffuser (setup #4)

2.3. Internal and external mass transfer theory

In the evaporation of solvents from a porous solid matrix, several physical processes occur simultaneously: the evaporation of the liquid phase, the transport of the solvent (either in liquid or gas phase) to the surface of the particle, and the transport of the gaseous solvent from the surface of the particle to the outside environment ([15], [16]). The liquid phase is generally considered to be in equilibrium with the surrounding gas, meaning that the evaporation rate is a function of the transport phenomena inside and outside the particle. The processes occurring within the particle (capillary flow, vapor transport, etc.) are called Internal Mass Transfer (IMT) [17], while those occurring in the empty spaces between particles are called External Mass Transfer (EMT). Since these processes occur simultaneously, the evaporation rate depends on the slower one, which becomes the limiting step. If convective air is used, two regimes can be identified [18]. At first, EMT is limiting (which means that it is slower than IMT), and the evaporation rate is roughly constant. This is called the constant rate period. As the solvent evaporates, its transport to the surface becomes increasingly harder [19], until a regime transition is reached and IMT becomes limiting. This is called the falling rate period, because the evaporation rate, which was kept constant during the constant rate period, decreases with time, representing an increasing resistance to the transport of solvent within the particles.

3. Results

A total of 21 experiments, divided into FP tests, tests with small masses and tests with big masses, are performed under different conditions. All experiments and the corresponding operational conditions are listed in the Table 3.

Table 3: Experiments in Flash Point Analyzer (FPA), standard TGA and TGA for big masses

	Run	**Set Up**	**Matrix**	**Conditions**	**m_i, g**	**m_f, g**	**DR_{MAX} (0÷5%) [%/min]**
Flash Point analyser	#1	FPA	Tissue	28 °C, P_{atm}, NMP on tissue, 17.3% w/w	0.31	\	\
	#2	FPA	Tissue	28 °C, P_{atm}, NMP on tissue, 18.3% w/w	0.31	\	\
	#3	FPA	Tissue	28 °C, P_{atm}, NMP on tissue, 29.1% w/w	0.37	\	\
	#4	FPA	Tissue	28 °C, P_{atm}, NMP on tissue, 44.1% w/w	0.46	\	\
	#5	FPA	Tissue	28 °C, P_{atm}, NMP on tissue, 47.5% w/w	0.50	\	\
	#6	FPA	Tissue	28 °C, P_{atm}, NMP on tissue, 50.0% w/w	0.51	\	\
	#7	FPA	Tissue	28 °C, P_{atm}, NMP on tissue, 58.6% w/w	0.62	\	\
Small masses	#8	standard TGA	S-CR1	50°C, P_{atm}, 200 ml/min N_2	0.17	0.15	0.35
	#9	standard TGA	S-CR1	70°C, P_{atm}, 200 ml/min N_2	0.21	0.18	0.60
	#10	standard TGA	S-CR1	90°C, P_{atm}, 200 ml/min N_2	0.17	0.14	1.16
	#11	standard TGA	S-CR1	22 °C (140 °C after 97 min), -0.5 barg	0.16	0.12	0.33
Big masses	#12	#1	S-CR1	28 °C, P_{atm}	5.04	4.70	0.06
	#13	#2	S-CR1	50°C, P_{atm}	5.20	4.3	0.63
	#14	#2	S-CR1	50°C, P_{atm}	15.2	12.7	0.31
	#15	#2	S-CR1	50°C, P_{atm}	52.4	43.1	0.17
	#16	#2	S-CR1	50°C, P_{atm}	101.1	88.0	0.05
	#17	#2	S-CR1	23°C, P_{atm}	51.2	47.2	0.01

	#18	#3	S-CR1	23°C, P_{atm}, stirring 50 rpm	51.5	47.8	0.05
	#19	#2	S-CR1	35°C, P_{atm}	52.2	47.2	0.07
	#20	#3	S-CR1	35°C, P_{atm}, stirring 50 rpm	52.3	44.2	0.13
	#21	#4	S-CR1	22°C, P_{atm}, 2 l/min air	51.8	45.3	0.11

*NMP = 1-Methyl-2-pyrrolidone (or N-Methyl-2-pyrrolidone)

3.1. Test in Flash Point Analyser

The correlation between solvent concentration in the solid and its flash point has been studied. FP measurements on solvents absorbed on solids have been carried out also in [20]: absorbent materials were proven to reduce the FP of all tested solvents. Furthermore, different types of absorbent have led to different increases in FP, by soaking all of them with the same quantity of toluene. In our case, the tested samples have been obtained by soaking equal pieces of tissue with different amounts of solvent. The solvent concentration on the solid has been calculated as a mass fraction. Each piece of tissue was 2.5 cm x 2.5 cm in size. Info on each test can be seen on Table 3. 1-Metyl-2-pyrrolidinone (NMP) was used as solvent. The results of tests 1 to 7 have been plotted in the graph of Figure 6, where the FP is plotted versus solvent concentration (w/w) in the tissue.

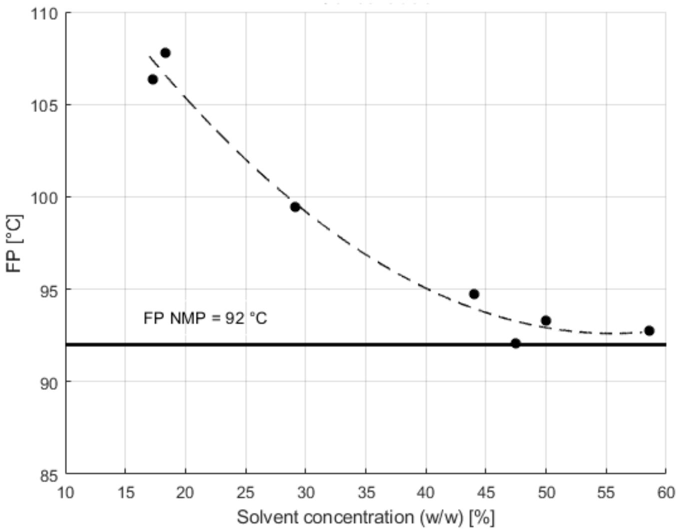

Figure 6: FP vs solvent concentration of the tests in the FPA

From the picture a correlation between FP and solvent concentration is recognizable: as the solvent concentration decreases, the FP tends to increase in a non-linear way. For higher values of solvent concentration, the FP tends to an asymptote, which corresponds to the FP temperature of the pure solvent (92°C). From this result, it can be noticed that as the solvent concentration in the solid decreases, the hazard decreases, so it becomes safer.

3.1.1. Relationship between WL, FP, VOCs

To evaluate the flammability hazard of a contaminated solid waste, its FP can be measured. However, the flash point cannot be easily evaluated with a continuous measurement. So, there is the need to correlate it with a quantity which can be measured continuously. To look for some correlations, an experiment was carried out in an open vessel, in ambient conditions. Here mass and FP have been measured with a sample time of 30 min. Desorbed VOCs have been measured continuously by a sensor. The results from this test can be seen in Figure 7. Here, it can be observed that the FP is proportional to a decrease in sample weight, which implies the desorption of the solvent. Also, as the solvent desorbs, the

VOCs signal keeps decreasing. This says that the velocity of desorption decreases as more solvent desorbs, since the VOCs signal describes the instantaneous desorption velocity. It can also be noticed that, with a weight loss of 5 %, the FP is already over 70 °C, which is a temperature that allows for the waste to be considered safe. From this observation, it has been decided to focus on weight losses until 10%, since this value is amply sufficient to ensure having a safe material.

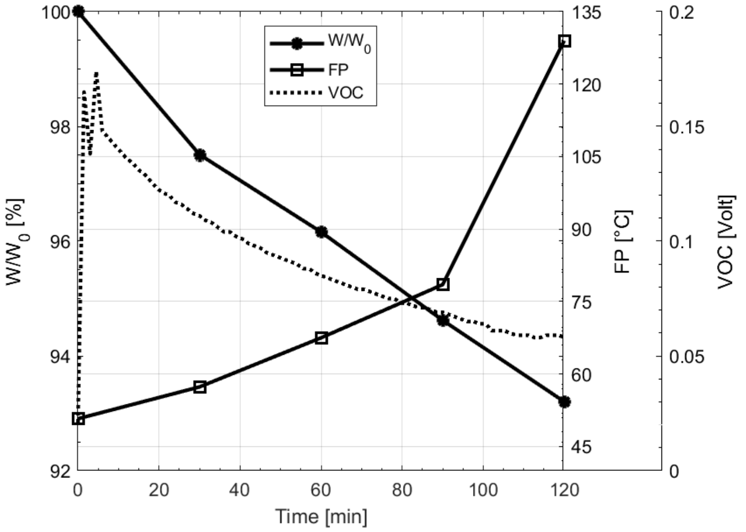

Figure 7: Normalized weight, FP and VOC signal vs time of the test in the open vessel

3.2. Tests with small masses in standard TGA

3.2.1. Effect of reaction temperature

Three experiments have been performed at different temperatures, from 50 to 90 °C. The results are visible in Figure 8 (left), where the normalized weight is plotted versus time. A horizontal line is plotted as well, which corresponds to a weight loss of 10%. This is because the focus of this research is a weight loss smaller than 10%, since, as already discussed, this is a sufficiently low value to have a safe material.

From Figure 8 it can be observed that temperature is a key variable in the desorption of solvents. The desorption velocity can easily be evaluated from the slope of the weight curve, with curves with steeper slopes corresponding to a faster desorption. Therefore, as temperature increases, the desorption becomes faster. To analyse the relation between temperature and desorption velocity, the desorption velocity at time equals zero versus temperature can be plotted. The result is presented in Figure 8 (right).

The relationship is not linear, but it seems to present an exponential behaviour. This could be explained by the fact that the saturation pressure increases exponentially with temperature, through Antoine equation. Indeed, desorption velocity depends on the solvent concentration at equilibrium in the gas phase, which is a function of solvent saturation pressure, expressed through the Antoine equation. This dependence goes into Raoult’s law, which describes equilibrium between composition in liquid phase and in gas phase.

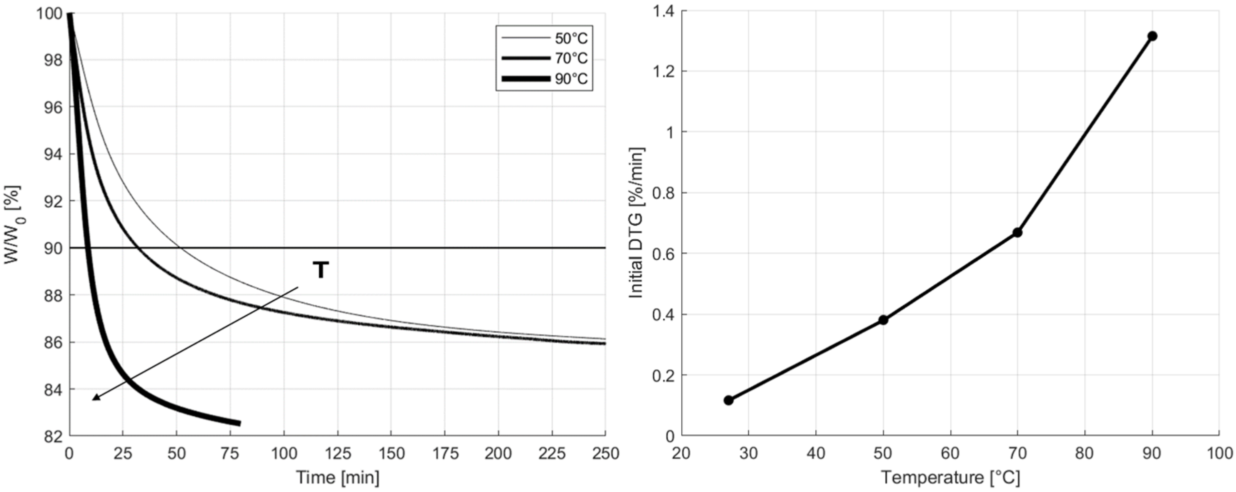

Figure 8: Normalized weight vs time (left) and desorption velocity, at time equals zero vs temperature (right)

3.2.2. Effect of the working pressure

The second analysed variable is the working pressure. Since in the literature the positive effect of vacuum for solvents desorption is widely described ([10], [15], [17]), a test in vacuum conditions has been carried out. The system was maintained at -0.5 barg, at ambient temperature (22°C). The normalized weight of this sample is plotted versus time in Figure 9 (left), where also the previous tests at different temperatures are plotted to have a better comparison.

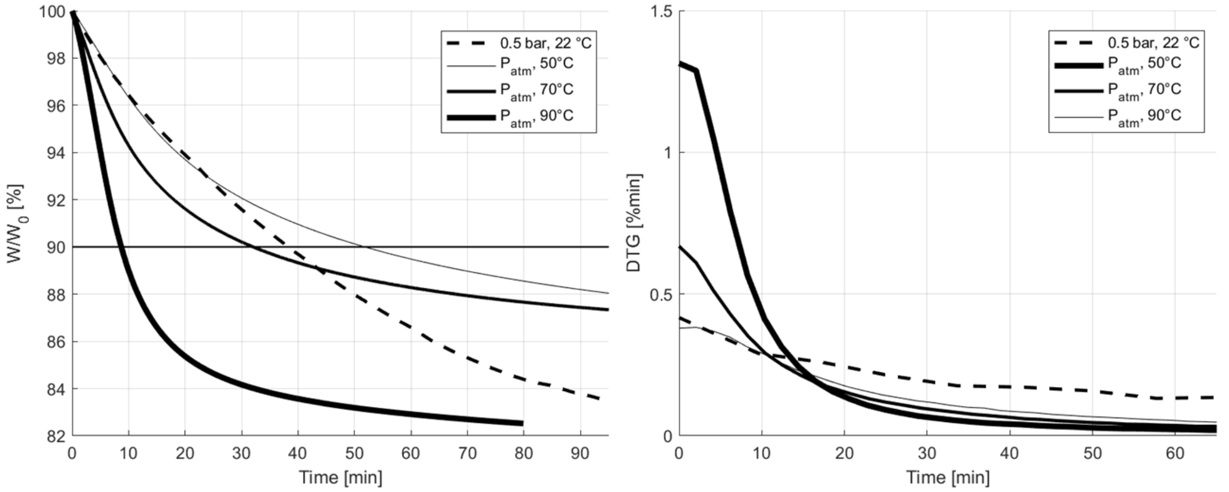

Figure 9: Normalized weight vs time (left) and DTG vs time (right), in vacuum conditions, at ambient temperature, compared with the three tests at different temperatures

By analysing the first part (from 0 to 20 mins), the desorption velocity in vacuum conditions, at 22°C, is the same as the one at 50°C, but at atmospheric pressure. Also, in vacuum conditions the desorption velocity slows down less than that at atmospheric pressure (see Figure 9 (right)), so, the velocity does not present a decay in the second part of the process, signifying a regime transition from EMT-controlled to IMT-controlled.

3.3. Tests with big masses in self designed TGA

3.3.1. Effect of the amount of treated mass

To analyse the effect of the sample mass, four experiments with different masses have been carried out. Masses range from 5 g to 100 g. All tests were performed at 50°C, in setup #2, in which temperature was controlled by an IR lamp. The samples were put on a cylindrical vessel, so they had the same exposed area. This way, by increasing the mass, the ratio between mass and exposed area increases, increasing the bed height. The normalized weights versus time of the four samples are plotted in Figure 10.

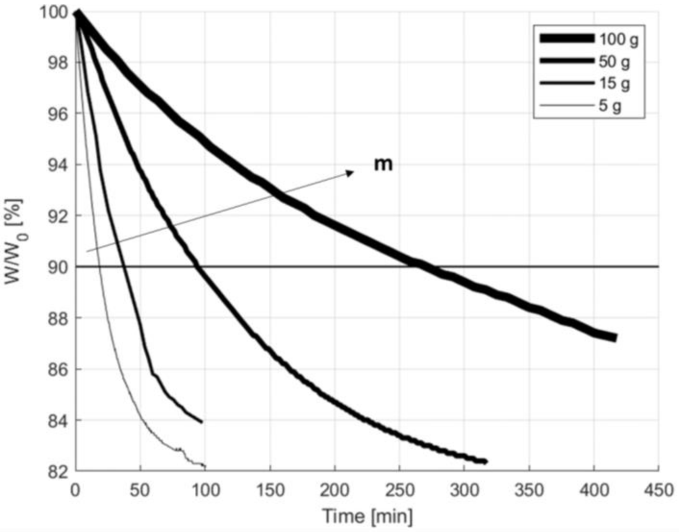

Figure 10: Normalized weight vs time of tests, with different masses

It is clear that the mass of the sample, and so the bed height, is a key variable for the solvent desorption. As the ratio between mass and exposed area increases, the desorption velocity greatly decreases. This reduction is due to the height of the bed, because inside it the only mass transfer mechanism is diffusion and diffusion through a long length is a very slow process.

3.3.2. Effect of stirring the solid

To have a faster desorption process, the mass transfer resistance in the bed needs to be reduced. To do so, the mass transfer mechanism in the bed can be changed from diffusive to convective, in order to reduce the influence of diffusion.
To achieve this, an axial impeller with two blades was used to stir the solid, in experimental setup #3. The ratio between impeller and vessel diameters is 0.82. The stirring speed was set to 50 rpm. Heating and stirring were cross-analysed in four experiments, with two of them at ambient temperature (23 °C), the other two at 35 °C, and one for each couple with stirring. For all four experiments, a sample of 50 g was tested. Unlike previous tests, the measurements are discontinuous, to avoid interference on the weight by the impeller. The normalized weight versus time of these four experiments can be seen in Figure 11.

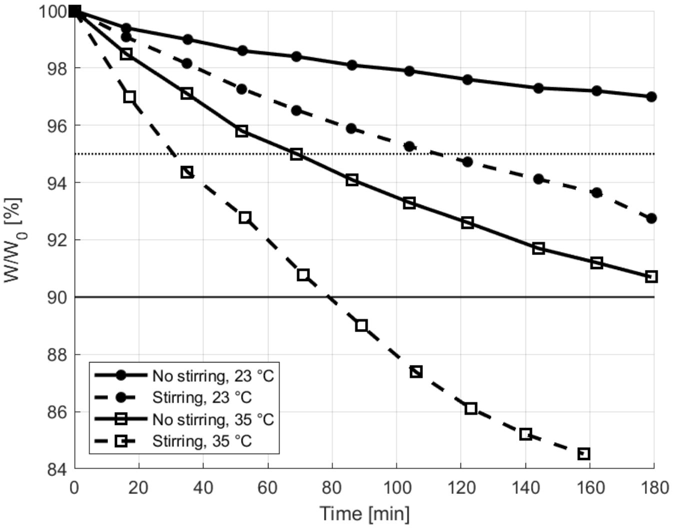

Figure 11: Normalized weight vs time of two stirred samples and of two non-stirred ones, at ambient temperature and at 35 °C

Stirring effectively improves the desorption process. This is because it improves contact between the material inside the bed and the surrounding air. This greatly reduces the diffusion length, improving the EMT. This suggests that EMT is indeed the controlling mechanism for these cases, and therefore improving it favours the desorption process.

3.3.3. Effect of the solid aeration

A second technology to reduce the EMT in the bed is its forced aeration. A sample of 50 g was aerated through a diffuser, at ambient temperature, with an air flowrate of 2000 ml/min. The solvent desorption versus time is visible in Figure 12, where the sample in aerated bed is compared to previously discussed tests.

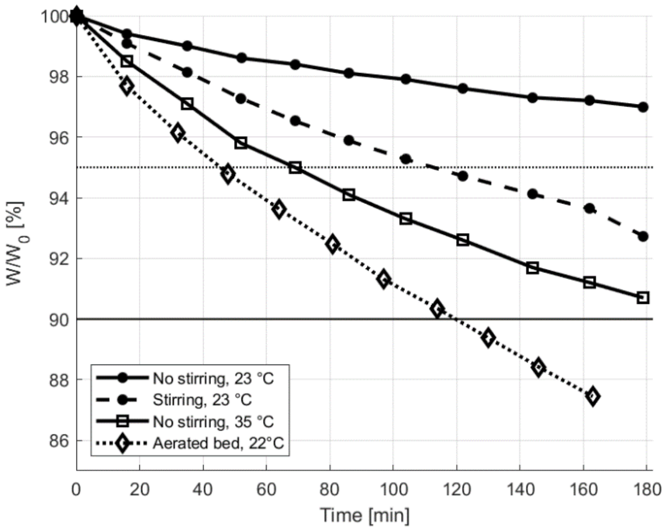

Figure 12: Normalized weight vs time in the aeration bed, compared with tests with and without stirring, with and without heating

Aerating the bed highly speeds up the desorption velocity. The aeration makes the process faster than the ones with heating or stirring. The good result obtained with aeration is due, as for stirring, to the improvement of the EMT in the bed. Indeed, aeration changes the mass transfer mechanism inside the bed from diffusive to convective. There is also an additional effect, compared to stirring: the air removes more solvent from the area around the particle, ensuring a high difference of concentration at the surface, which is the driving force of the desorption process.

4. Conclusions

The disposal of solid waste contaminated with flammable solvents can be critical in terms of safety. To find a route to reduce their hazard, several experimental setups have been implemented, which have allowed to understand the key factors in the desorption process. The safety of the material can be determined by measuring its flash point. However, since there is a correlation between flash point, weight loss and detected VOCs, the hazard of the material can be determined by simply measuring the integral value over time of the detected VOCs. This allows for a more continuous, simpler measurement in the reactor. Weight losses of about 7-10% are enough to increase the flash point over a safety threshold. So, the desorption results are analysed only up to this value. Working in vacuum conditions, a pressure of -0.5 barg leads to a desorption velocity, in the first period, like the one obtained with a moderate heating (50 °C) at atmospheric pressure. This is due to a higher diffusion coefficient around the sample holder in vacuum conditions, as well as the positive effect on the liquid-vapor equilibrium. In general, the most promising methods involve heating of the solid. However, as the mass increase, heating is not enough to desorb the solvent in a short time. Stirring is a good improvement for the desorption process, providing short desorption times, but the process is still slow if it is not coupled with heating and it presents a smaller desorption velocity than a test with mild heating (from 23 to 35°C). The bed aeration leads to fast desorption times, even at ambient temperature. In general, it stood out as the best technology when compared to stirring and to a mild heating, in terms of desorption velocity. In addition, this technology can be further improved by increasing the gas flowrate or by coupling it with heating.

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