FCC spent catalyst as an alternative reagent in Mo-contaminated hazardous waste enhanced stabilization

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Highlights

Sustainable substitution of traditional chemical reagents with a waste (FFC spent catalyst)

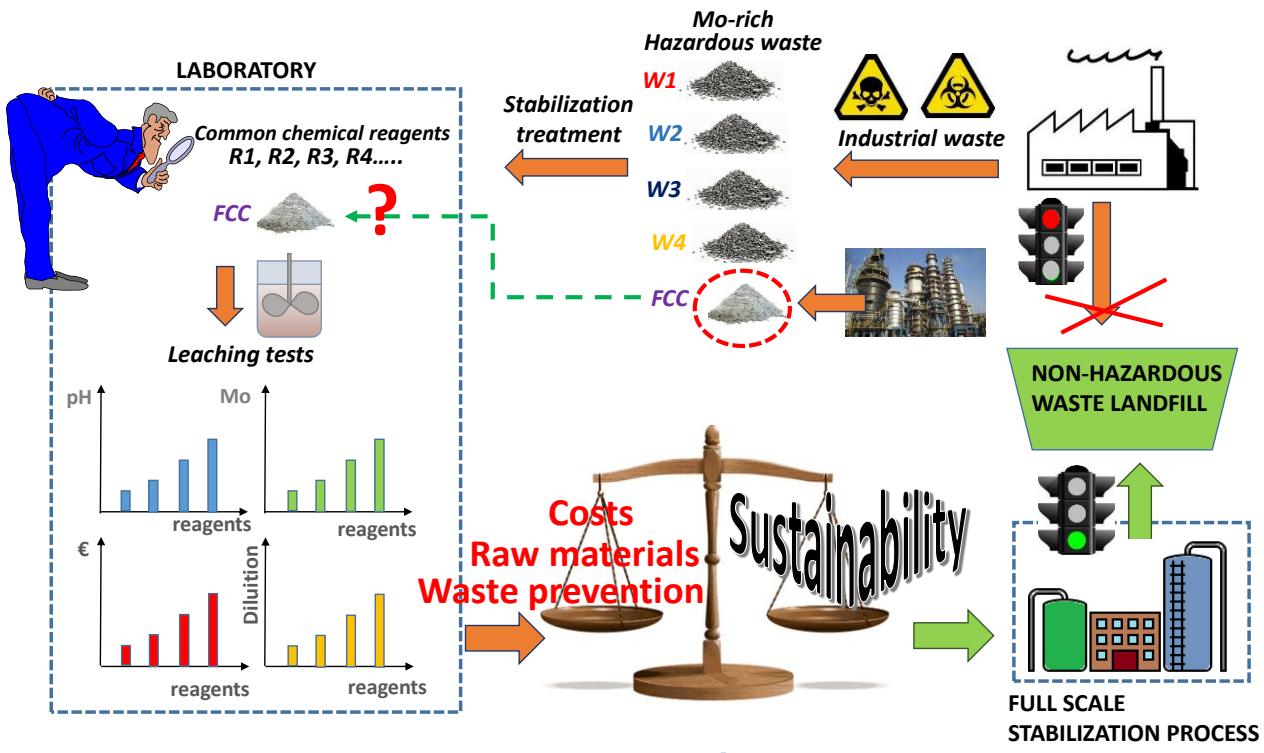
FFC spent catalyst is successful in limiting Mo release from hazardous waste

The use of FCC spent catalyst allows waste production prevention

A new approach is proposed to check and avoid dilution issues

The use of FCC spent catalyst allows significant industrial cost and environmental burden saving

Graphical Abstract



Abstract

Hazardous waste containing heavy metals must be stabilized through the addition of appropriate and costly chemical reagents before they can be safely disposed in non-hazardous waste landfill. Although effective, this practice can also significantly increase the waste final mass. This work focuses on the possibility of using another Mo contaminated waste, as an alternative reagent, to partially stabilise critical contaminant leaching trough chemical-physical interactions. Thanks to its unusual properties, spent fluid catalytic cracking (FCCSC) catalyst, classified as hazardous waste, was tested here as good candidate for Mo-contaminated waste partial stabilization. Results highlighted that FCCSC can be effective in drastically reducing the Molybdenum leaching below the legal limit for non-hazardous waste landfill disposal while significantly limiting the increase of the final mass of waste to be disposed with a substantial reduction of the industrial treatment cost, landfill volume requirement and overall environmental burden. By minimizing the waste to be landfilled, this research supports both the European directives and policies on sustainable waste management strategies and BAT (Best Available Techniques) for the treatment of industrial wastes within a circular economy framework.

Keywords: Molybdenum; hazardous waste; FCC spent catalyst; waste recovery; immobilization; stabilization

1 Introduction

Following the European waste management hierarchy, the best waste is that which is not produced, followed by waste that can be recycled or recovered (Mhatre et al, 2021). The full recovery of waste is always preferable (Khaertdinova et al, 2021). However, there is waste that, at present, cannot be sustainably recovered due to its intrinsic hazardous characteristics (Barton et al, 2020) and/or the high cost and impact of the recovery process.

Considering that landfilling is the final destination (Adami et al, 2021) we can still minimize the environmental burden by a waste stabilization process aimed at preventing/reducing the potential of long-term release of critical pollutants (primarily heavy metals and poorly biodegradable compounds). Two processes are mainly used to immobilize hazardous contaminants in waste: solidification and stabilization (Malviya et al, 2006). The first changes the physical properties of the waste to capture pollutants, generally using binders. As a result, there are no chemical modifications or elimination of pollutant species; in this case hazardous proprieties of the waste are maintained (Gliniak et al, 2020).

By contrast, stabilization includes processes that can change the chemical nature of contaminating species in hazardous wastes and shift the classification from hazardous to non-hazardous ones (Tisserant et al, 2017). This is mainly done through the destruction of organic pollutants and

conversion of hazardous inorganic species into others that are stable and not hazardous. The stabilization process can also be “partial” when the hazardous characteristic is not modified but the potential long-term release of the critical pollutants is sufficiently reduced (Meegoda et al, 2003).

These processes are also regulated by the best available techniques (BAT), recommendations on waste treatment, provided by legislation, in order to point out the cutting-edge technologies, both from an environmental and economic point of view.

The partial or full stabilization of waste is commonly performed using chemicals – acting as reagents and additives - which increases the process cost and the final waste production (up to 30-40%). Focusing on the principles of the circular economy, it would be more sustainable, when possible, to stabilize one waste material by the use of another waste with an equivalent proved effect, thus avoiding the exploitation of raw material (Ma, et al, 2020).

Studies on the use of waste or secondary raw materials for the stabilization of hazardous waste or contaminated soils (Wang, et al, 2021) have been presented in several researches (Watson-Craik, et al, 2020). Both organic (Maiti, et al, 2021) and inorganic (Hu, et al, 2021) waste have been proposed for heavy-metals contaminated-soil stabilization. The stabilization of hazardous waste contaminated by a single metal (e.g. cadmium or arsenic), were successfully performed using silica-derivate materials (Su, et al, 2018) (Duan, et al, 2021) while sewage sludge incineration ash was used for the co-stabilization of multiple metals (Ma, et al, 2020). Silica-rich waste materials were also used for the stabilization of metal-contaminated (Cu, Pb, Zn) fly ash (Li, et al, 2014) (Bosio, at al, 2013). The common feature that binds all these processes is the behaviour of silica (Imtiaz,et al, 2016).

Clays, consisting mainly of hydrated aluminosilicates belonging to the class of phyllosilicates, can also be applied in the waste stabilization process thanks to their electrostatic interactions, adsorption and cation exchange reactions with different metals and their derivative compounds. Due to their high surface area and porous structure (Otunola, et al, 2020) clayey materials have stimulated the study of modified or functionalized clays in order to increase the adsorbing capacity, also through the production of micro and nanocomposites (Gu, et al, 2019; Sarkar, et al, 2019). The required modifications can be achieved through physical processes such as grinding, thermal treatments or chemical processes (e.g. acid treatments, ion exchange reactions or functionalization with organic and polymeric molecules). Modifications are generally aimed at the removal or stabilization of one or more target metals in order to limit their environmental diffusion (Alrashidi, et al, 2020; Zhang, et al, 2021).

Similarly, natural zeolites (i.e. clinoptilolite) have been widely used for the removal of heavy metals from liquid wastes (Dosa et al. 2021). Their composition and porous nature have made them

candidates in several studies for the adsorbing of heavy metals through adsorption and ion exchange processes (Qasem, et al, 2021) (Zorpas, et al, 2021, Dosa et al., 2021).

It has been shown how various metals interact in diverse ways with zeolites where some metals are subtracted through cationic exchange processes, while others are trapped inside the porous cavities (Wei, et al, 2015). With regards to this last pathway, both the charge and topology of the material significantly influence the interaction with foreign species (M. Hong, et al, 2018, Piumetti, 2022). The simultaneous removal of various heavy metals is generally significantly related to a change in pH and conductivity, as an indication that the ion exchange process has taken place (Filatova, et al, 2016) (Tsai, et al, 2019).

Within this context, a hazardous waste such as fluid catalytic cracking spent catalysts (FCCSC) , which is made by zeolites supported on a high specific-surface silico-aluminate matrix, could represent an excellent candidate for its use as a stabilizer for heavy metal-contaminated waste.

The FCC conversion process allows high molecular weight hydrocarbons to be converted into a series of light molecular weight products (Al-Absi, et al 2018). In the process, the high-boiling point feedstock (generally heavy gas oil) meets the high temperature catalyst in the raiser reactor. The contact time feedstock-catalyst is about 2-4 seconds, after which the deactivated catalyst is separated from the mixture of hydrocarbon vapours by cyclones. The catalyst, partially deactivated, goes to the regenerator, where the coke on its surface is removed by partial or complete oxidation and the regenerated catalyst can be mixed over again with the feedstock (Occelli, et al, 2011). However, to maintain the quality of the required products, part of the catalyst needs to be replaced with fresh catalyst. There are currently around 400 FCC units in the world, consuming an estimated amount of catalyst of up to 840,000 tons; therefore, large quantities of spent catalyst need to be disposed every year (Vogt, et al, 2015).

In the FCC catalyst we find different forms of synthetic zeolites; The most commonly used are type X, type Y and ZSM-5 (Alotibi, et al, 2020). They are the primary catalytic components for selective cracking, significantly more active than the amorphous catalyst formerly used (Degnan, 2007). The silica-alumina ratio can vary, together with the addition of different additives, due to the operating conditions and the main target products (Belviso, et al, 2010).

The deactivation of the catalyst may be reversible or not. Irreversible deactivation reactions can take place inside the reactor due to the dehydroxylation reaction of the Brønsted acid sites, responsible for the catalytic cracking reaction or to the poisoning of the catalyst surface by metals contained in the feed (Cerqueira, et al, 2008). Spent catalysts are generally classified as hazardous, due to the contamination by heavy metals, coke and other elements (Fu, et al, 2021).

It is currently recognized that FCCSC represents not only a waste material, but also a resource, and its management has been extensively studied from the circular economy point of view (Alonso-Farinas, et al, 2020). Thanks to its proven pozzolanic properties (Payà, et al, 2003; Garcia, et al, 2007) FCC has been comprehensively investigated as a partial substitute for fillers in concrete or as an additive to cement mix (Al-Jabri, et al, 2021) (Da, et al, 2020). Interaction of FCCSC and asphalt binder were studied to improve high temperature mechanical properties and to limit the emissions of volatile organic compounds (VOCs) and leaching behaviour (Xue, et al, 2020). Moreover, studies have been carried out on the recovery of metals (mainly rare earths) from FCC waste (Sposato, et al, 2021) (Nguyen, et al, 2018).

Mo-polluted hazardous wastes, for their specific physio-chemical characteristics are hardly recoverable, even if some researches have been carried out in this field (Li, et al, 2016) (Zeng, et al, 2009), in the majority of the cases partial or fully stabilization appears to be the best environmental and economical option. Other alternatives include incineration (Mancini et al., 2014) and disposal in a hazardous waste landfill.

This research focuses on the stabilization of hazardous waste contaminated by Molybdenum. Due to its peculiar chemical proprieties the Mo co-stabilization with other metals is problematical because its solubility is inversely influenced by pH (and redox potential). At neutral pH generally the molybdate (Mo, VI) ions (e.g., MoO_4^{2-} and $HMoO_4^{-}$) are prevalent, though reduced Mo (V), such as MoO_2^{+} and $Mo_2O_4^{2+}$, are expected to coexist in reducing environments (Brookins, 1988) (Yang, et al, 2021). It was assessed that Mo stabilization can be performed using a reducing agent favours redox precipitation (Cantrell, et al, 1995) (Huang, et al, 2012). Notable stabilization results were also obtained using ferrous sulphate based additive on Mo-contaminated bottom and fly ashes (Mancini, et al, 2020). Ferrous sulphate acts both as a reducing agent and a pH-lowering agent, creating conditions in which the molybdenum compounds are less soluble. However, an acidic environment promotes the solubility of other heavy metals in the waste, which is a drawback in its use. The FCCSC waste, with its high specific surface silico- aluminate matrix, acidic attributes and pozzolanic properties, was tested here and compared to a more common raw product as an alternative reagent for Mo-contaminated hazardous waste stabilization.

1.1 Law and dilution issues.

Landfill for non-hazardous waste may also accept “stable, non-reactive hazardous waste” (e.g., solidified, vitrified, etc.), which means hazardous waste with leaching behaviour equivalent to those of non-hazardous waste. Waste must accomplish the requirements set out in Annex II of the European directive 1999/31/CE and European directive 2003/33/CE. Important requirements for the “stable,

non-reactive hazardous waste" acceptance into a non-hazardous waste landfill are a total organic carbon concentration (TOC) less than 5%, pH higher than 6, dry matter content higher than 25% and a positive evaluation of ANC/BNC (Acid Neutralization Capacity/Base Neutralization Capacity). The treated waste must also show appropriate geotechnical properties according to the "Waste Acceptance at Landfills" of UK Environment Agency, and specifically: Californian Bearing Ratio (CBR) > 5% (Method BS 1377:1990 or EUROCODE 7) for non-cohesive waste and a shear strength > 50 Kpa (Method ISO/DIS 22476-9:2014) for cohesive waste.

A further fundamental legal requirement, when mixing various waste during the stabilization treatment, is imposed by Directive 1999/31/EC and 2003/33/EC, that forbids mixing waste with the sole purpose of meeting the waste acceptance criteria in landfill (i.e. by dilution).

Given that a certain amount of dilution is inevitable, there is not an official or recognized method to define and determine analytically the maximum admitted dilution ratio and its effect on the final admissible concentration in the eluate from the leaching test.

The authors (Mancini, et al, 2020) proposed a simplified method to estimate dilution contribution in waste stabilization treatment involving a limited number of waste and chemical reagents to ensure the verifiable prevalence of the treatment over the dilution effect.

The method evaluates - through a weighted mean - all the leachable mass of the pollutants from each of the waste and chemical reagents involved in the stabilization process by considering their separate release of target pollutants as measured by the leaching test. The concentrations of the target pollutants in the leachate from the treated (mixed) waste are then measured and compared with those expected - as mathematically obtained values - to be intended as "pure" dilution effect.

It is required that the values of the measured concentrations are significantly lower (2 fold) than the expected concentration values considered as "simple dilution" to assess the efficiency of the stabilization treatment and environment protection.

2 Materials and Methods

2.1 Materials

Industrial solid waste was collected as composite sample (10 samples of 1 kg for each of 4 waste, collected during one month of operation). This was then mixed and quartered obtaining sub-samples of 100 g which were finally used for the stabilization experiments. No pre-treatment (e.g. sieving) was applied on the sub samples due to the nature of the waste (Table 1). Samples were stored at room temperature before analysis. FCCSC was provided by the ENI S.p.A. refinery located in Milazzo (Sicily-Italy) where FCC use is related to the production of naphtha and gasoline.

Chemical reagents used for the waste stabilization are calcium oxide (technical grade), Portland pozzolanic cement (technical grade), a commercial ferrous sulphate-based additive (©Venator Materials PLC), a concentrated liquid solution of ferrous chloride (30% of purity), barium chloride (lab grade 99%), sulphuric acid (lab grade 98%), oxalic acid (lab grade). Reagents used were not always lab-grade because this study refers to an industrial-scale waste treatment, so considering actual industrial procedures also to check the real economic feasability. Table 1 reports the European Waste Catalogue (EWC) - waste codes and related physio-chemical characteristics, including Molybdenum concentration in the leachate, of all the industrial solid wastes examined in this study. It should be noted that other chemical species showed concentrations above legal limits in the leachate of the non-treated wastes: SO_4 in waste 2, Cl^- and TDS (total dissolved solids) in waste 3, Cl^- and TDS in waste 4 and Sb in FCCSC, respectively. The analysis of these parameters and their variation through various treatments goes beyond the purpose of this work. In Table 2, are presented the hazardous characteristics and chemical species responsible for the hazardousness of the treated waste and FCCSC.

Table 1 Wastes in the waste stabilization tests

	u.m.	Waste 1	Waste 2	Waste 3	Waste 4	FCCSC
Description		sludges produced by groundwater remediation	spent catalyst from deNOx baskets	sludges produced by wastewater treatment plant	bottom ash produced by incineration plant	Spent catalyst from naphtha production
EWC		190304*	160802*	100120*	190111*	160807*
status		sludges	powder	sludges	powder	powder
pH		>12	8	8,5	>12	6.8
Humidity	%	40	10	35	5	2
Mo (leachate)	mg L^{-1}	2.53	2.8	4.83	1.98	0.8
Mo	mg Kg^{-1}	33.6	1870	24.8	100	147
As	mg Kg^{-1}	<5	67.7	<5	8.6	<5
Ba	mg Kg^{-1}	28.1	125.9	14.1	187	<5
Cd	mg Kg^{-1}	<5	<5	<5	<5	<5
Total Cr	mg Kg^{-1}	31.8	485	11.5	67.1	32
Cu	mg Kg^{-1}	32	32.3	12.1	676	36
Hg	mg Kg^{-1}	<5	<5	<5	<5	<5
Ni	mg Kg^{-1}	232.9	199.6	280	156	1869
Pb	mg Kg^{-1}	<5	13	<5	116	81
Sb	mg Kg^{-1}	<5	<5	<5	139	<5
Se	mg Kg^{-1}	<5	<5	<5	<5	<5
Zn	mg Kg^{-1}	85.8	53	90	4116	84

Table 2 Hazardous properties and characteristics for each waste stabilized

	Waste 1	Waste 2	Waste 3	Waste 4	FCCSC

Hazardous Properties	HP7, HP11, HP14	HP14	HP4	HP7, HP14	HP7
Hazard statement	H350i, H341, H410	Cautionary	Cautionary	H350i, H410	H350i
Hazard class and category	Carc. 1A, Muta.2, Aq. Chronic 1	Assigned by producer	Assigned by producer	Carc. 1A, Aq. Chronic 1	Carc. 1A
Chemical species	NiO, V_2O_5, ZnO	/	/	NiO, ZnO,	NiO

2.2 Methods

All the hazardous industrial waste were treated through different combinations of chemical reagents including the FCCSC (here considered both as a reagent and as a waste). The characterization of all the waste was carried out by determining metal concentration in the solid and in the eluates from leaching tests. The solid characterization was performed through an acid attack according to UNI EN 13657. Briefly, a solid sample of 2 g was transferred to the digestion vessel where 28 mL of aqua regia was added to dissolve metals content in the sample. The mixture was kept at 120 °C for 2 hours in a digestion system model SPB 50-24 from Perkin Elmer and then filtered through filter paper and brought to a volume of 50 ml. Metals in the digested samples were detected according to UNI EN ISO 17294-2:2016: samples were acidified by super pure nitric acid (69%) and analyzed after the opportune dilutions (1:20) by ICP mass (nexION 350x - Perkin Elmer).

Each stabilization test involved the addition of a weighted amount of sampled waste and reagents according to the ratio reported in Table 3. Then, after adding 20-30 mL of distilled water, the whole mass was mixed carefully in order to achieve the highest homogeneity. Finally, the sample was left to mature for 24 hours with periodic agitation and light ventilation. After maturation was completed, the leaching tests were carried out, based on a solid-to-liquid ratio of 1:10. Humidity of the sample was determined using a thermal balance (Ohaus MB90). The mix was left in agitation in an overhead shaker (Heidolph model Reax 20/8) for 24 hours at 9 rpm. The solution was then filtered twice - first through a pleated filter and then through a 0.45 µm PES filter - in order to obtain an eluate to be analyzed. When needed the samples were pre-centrifuged (Thermo SL16). Metal detection was performed according to UNI EN ISO 17294-2:2016 as previously described. An aliquot of the eluate was used to determine pH values for all the samples (Crison pH-meter basic 20+). For all procedures, purified distilled water was used (Millipore Milli-Q lab water system). Each experiment was performed in triplicate.

Table 3 Reagents in the waste stabilization tests

Treatments	Waste 1	Waste 2	Waste 3	Waste 4
T1	50% FCCSC+ 1% $BaCl_2$	5% $FeSO_4$ + 1% $FeCl_2$	50% FCCSC+ 2% FeSO4 + 2% $FeCl_2$	2% $FeSO_4$ + 30% FCCSC
T2	15% $FeSO_4$ + 4% $FeCl_2$	50% FCCSC+ 1,5% $FeCl_2$	10% $FeSO_4$	13% $FeSO_4$ + 2% $FeCl_2$
T3	2% CaO + 15% $FeSO_4$	10% $FeSO_4$	1% $BaCl_2$ + 5% Oxalic acid	12% $FeSO_4$
T4	30% Portland cement	1% Portland cement + 4,5% $FeCl_2$	35% Portland Cement	5% $FeSO_4$
T5	20% H_2SO_4 (48%)		5% CaO + 5% Cement + 10% $FeSO_4$	

3 Results and discussion

Results from the series of treatments of the four waste are presented in Figures 1 to 4. Figure 1 shows the pH as measured for each waste and stabilization treatment, while Figure 2 shows the corresponding Mo release in the eluate. All the results in the Figures 1-4 are ordered in terms of increasing molybdenum release to the eluate.

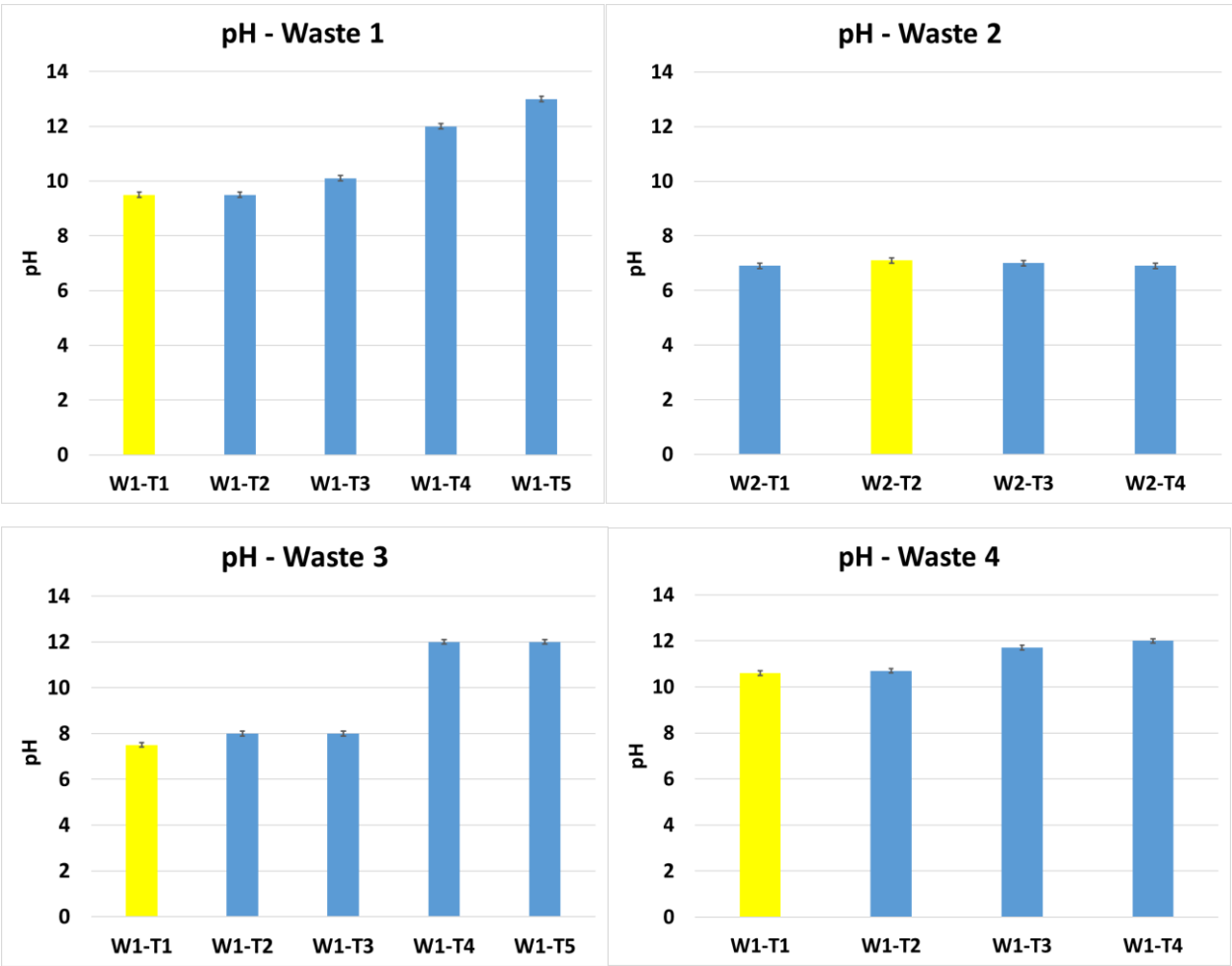
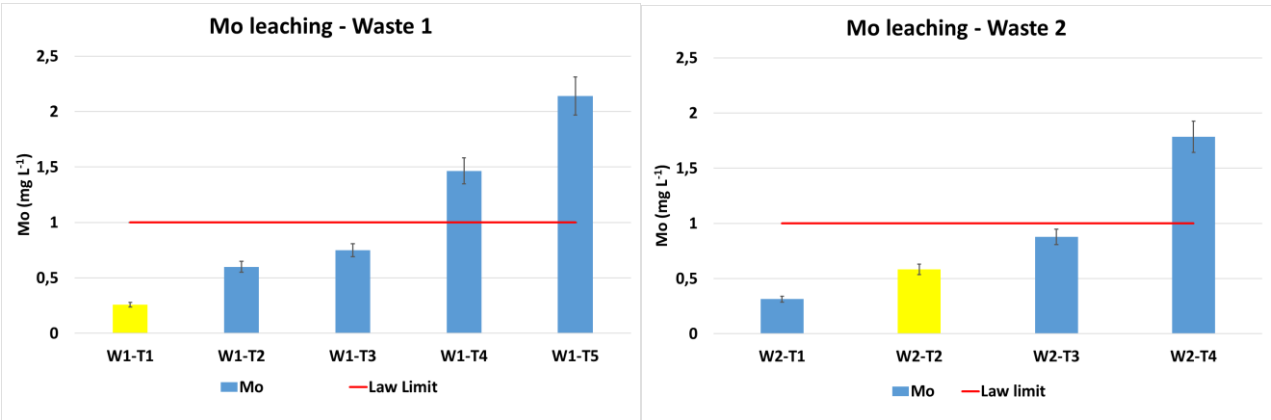


Figure 1. pH values in the eluates from the leaching tests of the treated wastes (yellow bar refers to the FCC stabilization treatment)

As already highlighted in Mancini et al. 2020 and confirmed by other research (Izquierdo, et al, 2012) (Tsai, et al, 2019), molybdenum builds a strong pH-dependence with its own water solubility, generally showing an increasing molybdenum release with the leaching solution pH increase (Mohammad, 2017). This behavior is confirmed by the FCCSC-treated waste (yellow bar) showing the lowest pH, generally resulting in the lowest Mo leachability. This is due to the acidic content of the FCCSC, which sets its own pH around 6. Previous studies of the authors (Mancini et al. 2020) also highlighted the importance of pH and redox potential in molybdenum solid waste treatment and metals contaminated soils (Luciano et al., 2013). There are however other mechanisms which affect Mo solubility in the case of FCCSC-treatment which are related to the adsorption of heavy metals on the sorbent phases of silico-aluminate matrices within the FCCSC (Langmuir, et al, 2004). These matrices are characterized by a wide-ranging distribution of pores which act as sites for electrostatic interactions (Van der Waals forces) between positively charged areas of the catalyst and the negatively charged oxoanionic compounds of molybdenum (such as molybdate). These interactions noticeably reduce molybdenum leachability, trapping its compounds in the pores of the matrix. This additional contribution may explain why the molybdenum release is far lower in FCCSC treated waste in comparison to other treatments, even showing comparable final pH such as in the waste 2 and waste 4 treatment tests.



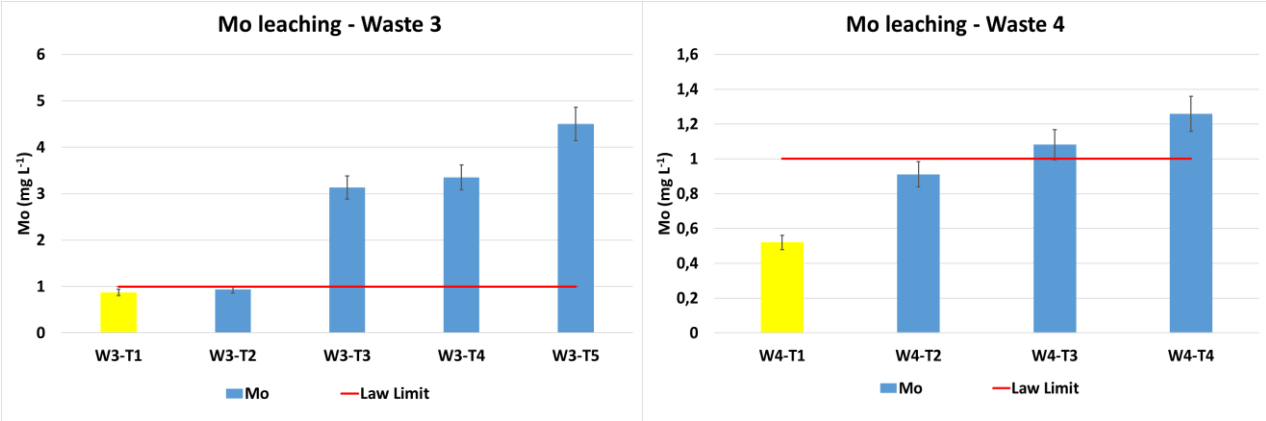
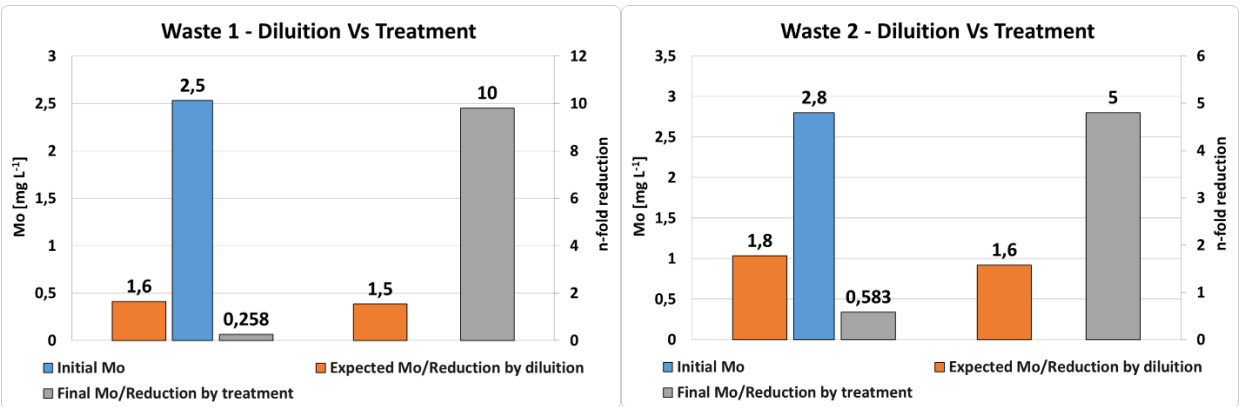


Figure 2 Molybdenum in the eluates from the leaching tests of the treated wastes (yellow bar refers to the FCCSC stabilization treatment)

Figure 2 also shows the Mo concentration legal limit (the red line) in the eluate for waste disposal in a non-hazardous waste landfill. For all the experiments Mo concentration in the leachate of the waste treated with the addition of FCCSC (yellow bars) was always lower than the disposal limit in non-hazardous waste landfill. This shows as the use of FCCSC is particularly effective in the partial stabilization of one of the more complex pollutant (Izquierdo, et al, 2012) to be managed in hazardous solid waste treatment.

Another important result that was obtained through the FCCSC was that the combined treatment offers the opportunity to simultaneously treat two different waste, with a huge increase in the treatment efficiency, reduction in the costs and reduction in the overall impact of the process on the environment. This last due to the minimization of the overall waste produced and the natural resources consumption. Lastly, all the described FCCSC treatments were all compliant with landfill disposal law requirements.



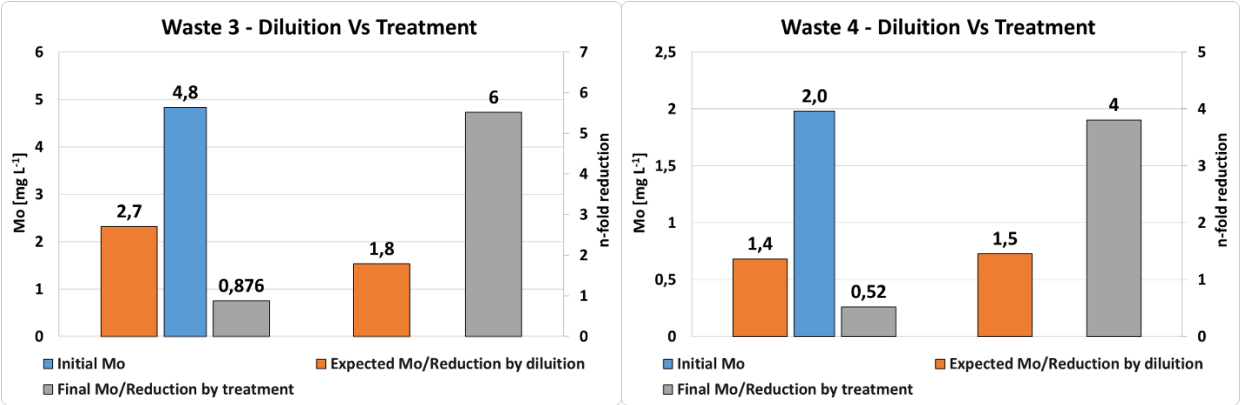


Figure 3 Mo concentration (left) in the eluate from the leaching test of untreated (blue bar), treated (grey bar) and expected by dilution (orange bar) and comparison (right) of the expected and real n-folder potential mass reduction of Mo release to the environment.

According to the approach proposed by Mancini et al, 2021, Figure 3 shows (left side of each picture), for each of the stabilization treatments of the four waste utilizing FCCSC as main reagent, the comparison between: 1) the Mo initial concentration in the leachate of the waste (blue bar), 2) the one expected (orange) by simple dilution and 3) the real (grey) concentration measured after the combined treatment with FCCSC. As already observed, FCCSC was able to decrease Mo solubility below the law limit of 1 mg L^{-1} in all the stabilization tests of the four waste, although they show different physical-chemical characteristics.

On the contrary, in neither of the experiments with the 4 different waste the Mo expected concentration is lower than the law limit, confirming that the landfill disposal of the waste cannot be achieved by “simply mixing” the different waste.

Figure 3 also shows (right side of each picture) the n-folder reduction of the Mo mass potentially releasable in the leachate from each treated waste comparing the “pure” dilution contribution and the overall effect of the treatment. As previously highlighted, this further verification is required by waste regulations - although non standardized yet - to avoid the disposal of hazardous waste in the environment without an adequate and effective treatment. In comparison to simple dilution, the whole treatment process is effective in reducing the burden to the environment by up to 6.7, 3.1, 3.3 and 2.7-fold, for W1, W2, W3 and W4, respectively. Overall, results showed in Figure 3 confirm that, accordingly to the proposed verification criteria, the dilution contribution to Mo abatement in the leachate is limited - for all the FCCSC-waste treatments - and cannot be considered as the main factor in achieving the waste stabilization disposal goal.

The cost of reagents as estimated for the industrial-scale treatment of 100 tons of waste are shown in Figure 4, for each of the tested waste.

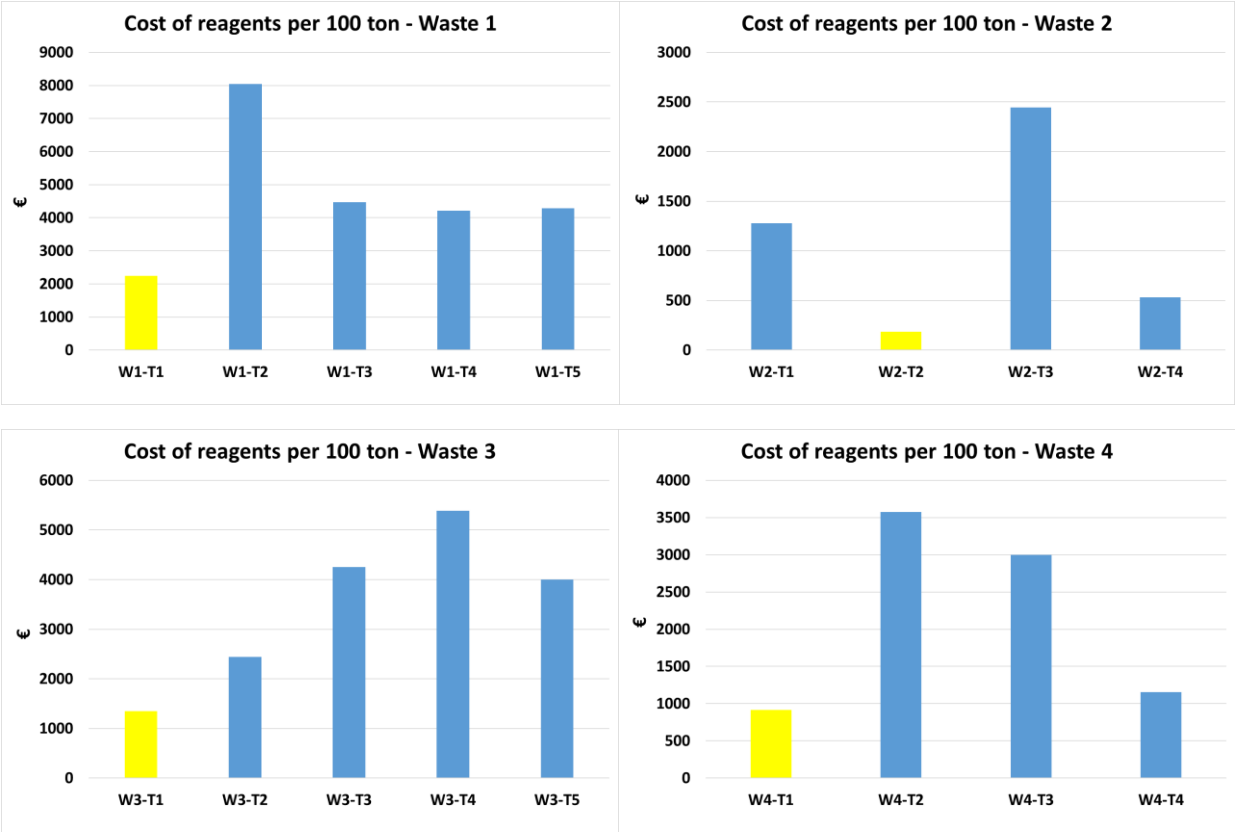


Figure 4 Cost of reagents for treatments referred to 100 tons of waste. (Yellow columns represent treatments with FCCSC.).

The yellow bar still represents the FCCSC treatment showing as the combined treatment of the two waste dramatically decreases the overall demand and cost of reagents as most of the complex chemical interactions - in Mo stabilization - is now produced by the FCCSC waste as above discussed. It should be noted, in the stabilization treatment with FCCSC, that FCCSC itself is a waste "on the market" (thus requiring a stabilization process for the final disposal). As a consequence, its cost as reagent is not computed in the combined treatment with the other wastes.

The reduction of the process costs, shown from the results in Figure 3, is an additional (but important) benefit, in terms of circular economy, from the combined use of FCCSC in hazardous waste stabilization, providing further economic and environmental sustainability - at an industrial scale - due to the relevant reduction of the pure chemicals involved in the process.

Another economic and environmental benefit from the proposed approach, is due to the not negligible reduction of the total mass of waste disposed and the consequent saving in landfill volumes.

This last result is better shown in Figure 5 where the colored bars represent the mass increase - as a percentage of the initial mass of the waste - due to the addition of the reagents and the overall physio-chemical effect of the treatment.

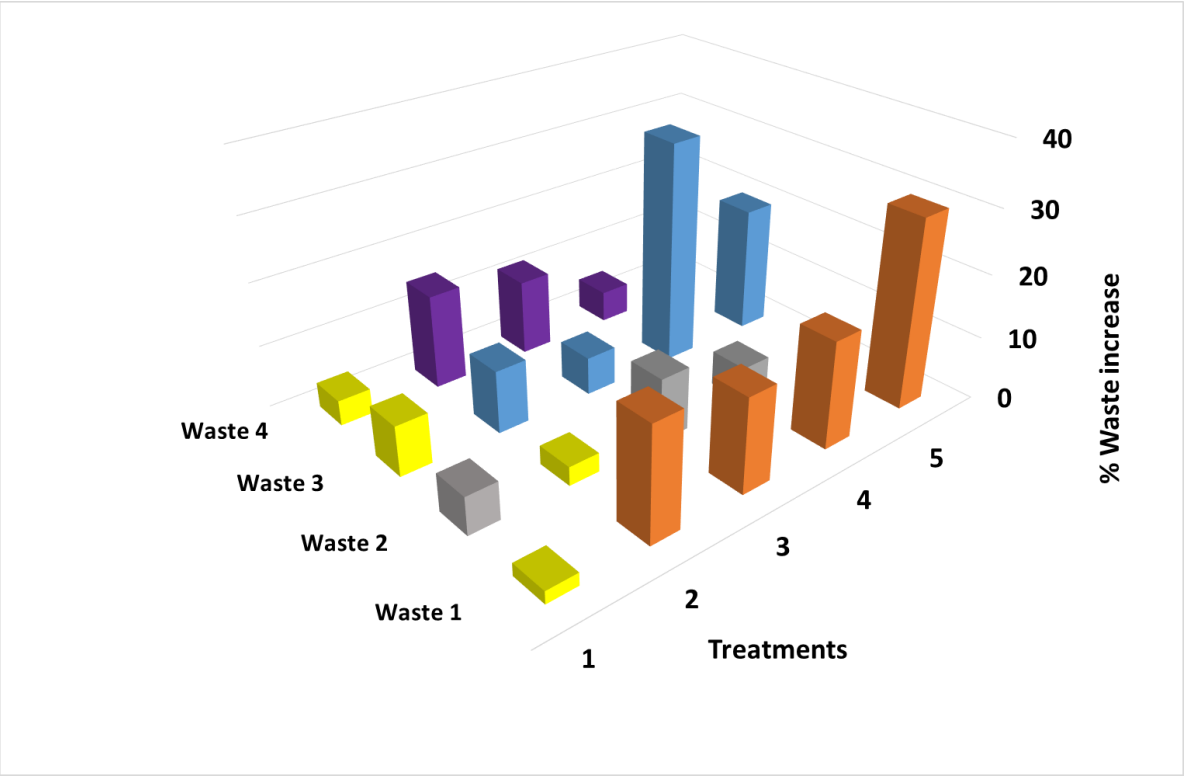


Figure 5. Waste increase (%) as effect of the stabilization treatment. The yellowbars refer to the FCC use as reagent.

Each color stands for a waste treatment; the yellow bars again identify the FCCSC-waste combined treatments. The latter show how the proposed approach can minimize the waste increase for all the waste/treatments except for W3-T3 where the increase of the final waste mass is lower than the corresponding treatment with FCCSC. However, it can be gathered, thanks to the combined information from Figure 4 and Figure 1, as the W3-T3 treatment causes a total cost of reagents significantly higher (40 €/ton) than the corresponding FCCSC treatment (W3-T1, 12 €/ton) while not allowing the stabilization/disposal goal. When considering, as an indicative value, a price on the market of 200-300 €/ton of hazardous waste for the overall process of waste stabilization and landfill disposal, a saving in 10% in the waste increase and related landfill volume saving can be assumed as relevant as the highlighted saving in the reagent cost.

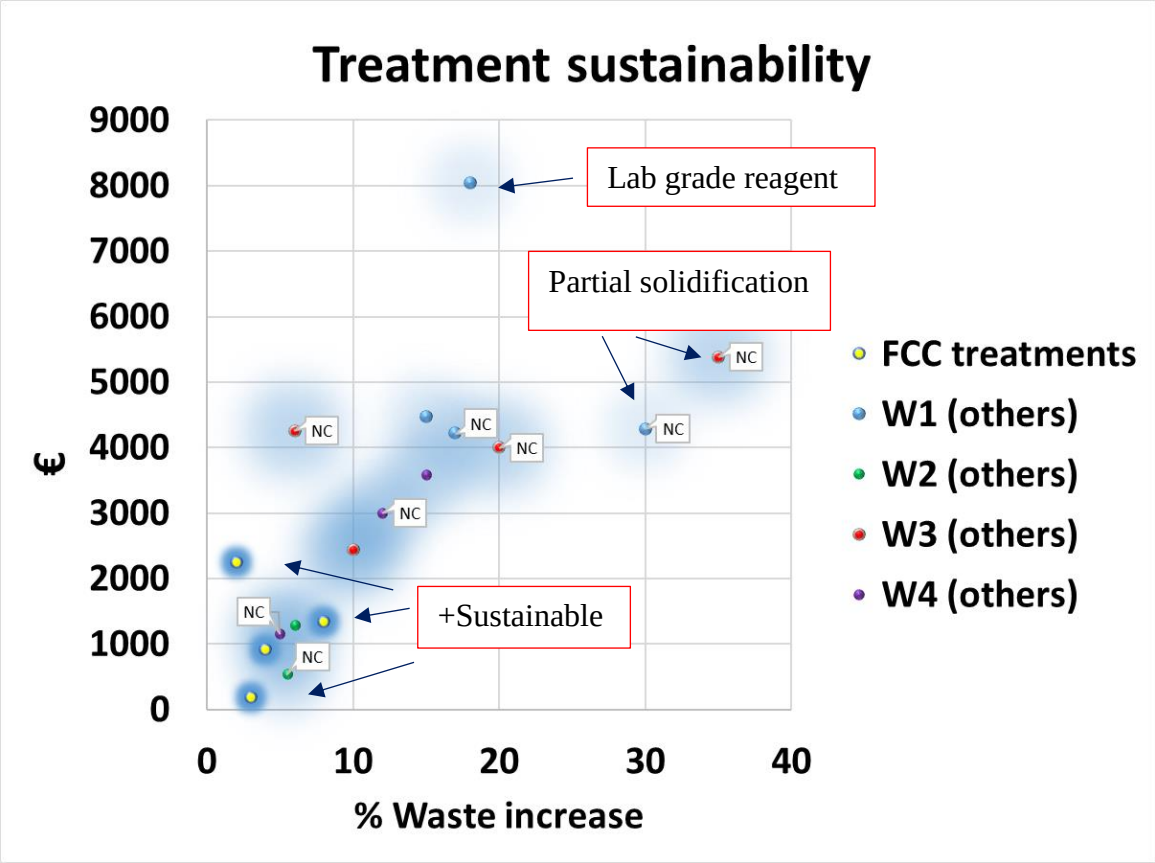


Figure 6. Comparison between reagent costs and waste increase for the different treatment. (NC= Not compliant)

In Figure 6 the different treatments are plotted against the reagents' costs and the percentage of waste increase. It can be seen that FCCSC-waste treatments (W2-T2, W4-T1, etc.) are all positioned close to the origin of the two axes as they both show low reagent cost and percentage of waste increase, which are the more sustainable conditions from both the economic and environmental perspectives.

Most of the other treatments in Figure 6 (e.g. W3-T5, W1-T2, etc.) require a higher cost of reagents but also a higher waste increase; besides most of them are not compliant with law limits, as specified by the label "NC". The high cost and waste increase are however common when dealing with hazardous waste with different pollution sources that therefore require treatment by a more complex mix of reagents. The cost of specific reagents could also vary dramatically depending on availability on the market, current demand, purity and transportation costs. This may explain why most treatments are carried out using cement, calcium oxide and ferrous sulphate which are generally more readily available on the local market and are consequently cheaper than other pure chemicals.

There is a small area (W1-T5, W3-T4) on the right of the diagram which refers to treatments involving high dosages of reagents with a medium cost, causing a very high waste increase: this is the area of partial-solidification which is usually performed using a huge amount of low cost cement (around 80€/ton). However, this treatment solution is not particularly efficient with oxoanionic pollutants such as molybdenum and is unfavorable from both an economic and environmental point of view, so it

should be avoided. A notable case is the treatment (W1-T2) showing a medium value of waste increase but the highest cost of reagent. Although highly effective in minimizing the Molybdenum release, it involves chemicals with high purity and scarce availability on the market, making this treatment clearly efficient from a chemical point of view, but totally unacceptable for industrial applications.

4 Conclusions

The comparison of several reagent combinations to partially stabilize different Mo-contaminated industrial hazardous waste clearly showed that the use of FCCSC - a waste coming from a fluid catalytic cracking process for naphtha production - can effectively substitute traditional reagents in inhibiting the release of Molybdenum below the legal limits for the resulting stabilized hazardous waste disposal into a non-hazardous waste landfill. The unique chemical-physical characteristics of FCCSC allows Molybdenum to be trapped within the catalyst microstructure, thus inhibiting and decreasing its release into the environment. The combined use of FCCSC as reagent/waste also allows a noteworthy saving of raw materials, thereby limiting the overall mass of waste from the stabilization process, with resulting environmental benefits. Furthermore, waste treatment costs are significantly reduced by both the savings in the addition of the reagent (around 100-200%) and by the reduction in the final landfill volume consumption.

Although the chance of using FCCSC as an alternative reagent in the hazardous waste stabilization process must be carefully checked - case by case - against the highly variable physio-chemical characteristics of different wastes, results from present research, where four waste were positively investigated, provide important insight into FCCSC capability of immobilizing Molybdenum, within this specific application. This research, by providing an alternative approach to the stabilization of hazardous industrial waste polluted by heavy metals, also promotes the safe, efficient and sustainable combined treatment of different hazardous waste within a circular economy perspective, thus tangibly supporting European directives and policies on sustainable waste management strategies and BAT (Best Available Techniques) for the treatment of industrial wastes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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