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Reuse of Hydrocarbon-Contaminated Sludge from Soil Washing Process: Issues and Perspectives

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Soil washing is a remediation technology commonly used to treat soil contaminated by total petroleum hydrocarbons (TPHs) (Seyed Razavi et al., 2012). Nowadays in Italy there are about ten plants, mainly placed in the north of the country. After treatment, coarse materials (i.e. gravel and sand) are cleaned and can be reused, e.g. as aggregate for concrete production; contaminants are concentrated in the filter-pressed sludge containing fine grains (i.e silt and clay), which is usually landfilled.
This paper analyses different alternatives for sludge reuse at an industrial scale in Italy; the main normative and technical constraints are presented and discussed. In addition, the preliminary results of a lab-scale experimentation aimed at investigating the treatability of soil washing residues by wet oxidation are presented.
The reuse and valorisation of soil washing originated sludge is desirable not only from the economic point of view but also because Italian and European legislation put waste recycling as a priority. Several tens of thousands of tons of sludge are produced and landfilled in Italy every year; they represent materials which could be exploited at industrial scale in place of virgin silt and clay to produce stabilised soil for road construction or bricks in brick works. Sludge reuse for cement production is possible, too, but it is probably more expensive.
The use of raw sludge produced in soil washing plants implies a potential risk of environmental contamination therefore the basic condition for sludge recovery and reuse is its decontamination, which can be theoretically obtained by thermal desorption, solvent extraction or chemical oxidation. Wet oxidation tests executed by the authors indicate that such a process is potentially applicable. 98 % removal efficiency of TPHs was obtained in a lab-scale reactor setting temperature, treatment time and initial oxygen pressure to 250 °C, 30 min and 20 atm, respectively. Further tests will be carried out in order to identify the most favourable and cheapest treatment conditions.

1. Introduction

Soil washing is a remediation technology commonly used to treat soil contaminated by total petroleum hydrocarbons (TPHs). Nowadays in Italy there are about ten plants, mainly placed in the north of the country. After treatment, coarse materials (i.e. gravel and sand) are cleaned and can be reused, e.g. as aggregate for concrete production; contaminants are concentrated in the filter-pressed sludge containing fine grains (i.e silt and clay), which is usually landfilled.
Sludge landfilling weighs a lot on the operational costs of a soil washing plant, up to 50 % (Piepoli et al., 2010); soils conveniently treated in those plants should contain percentages of fine grains inferior to 30 % w/w (Vaccari et al., 2005). The current cost for waste landfilling (including the transport to the landfill, as well) varies between 60 €/t (in landfills for non-hazardous waste) and 90 €/t (in landfills for

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hazardous waste). A soil washing plant receiving contaminated soils whose moisture is 10 - 20 % and silt/clay content is 20 - 30 % produces 215 - 415 kg of sludge per ton of soil treated (assuming that the moisture of filter-pressed sludge varies between 25 and 35 %). It means that nowadays the cost for sludge landfilling in Italy varies between 15 and 35 € per ton of contaminated soil treated in the plant.
The reuse and valorisation of soil washing originated sludge is desirable not only from the economic point of view but also because several tens of thousands of tons of sludge are produced and landfilled in Italy every year.
This paper analyses different alternatives for sludge reuse at an industrial scale in Italy; the main normative and technical constraints are presented and discussed. In addition, the preliminary results of a lab-scale experimentation aimed at investigating the treatability of soil washing treatment residues are presented. In fact, sludge reuse presupposes its decontamination; rapid and effective TPHs removal can be theoretically obtained through three different processes: solvent extraction, thermal desorption, chemical oxidation.
Solvent extraction is a common form of chemical extraction using an organic solvent as the extractant. Organically bound metals can be extracted along with the target organic contaminants, thereby creating residuals with special handling requirements. Traces of solvent may remain within the treated soil matrix, so the toxicity of the solvent is an important consideration.
Low temperature thermal desorption (LTTD) is a full-scale technology that has been proven successful for remediating petroleum hydrocarbon contamination in all types of soil. In LTTD, soil is heated to between 90 and 320 °C. Contaminant destruction efficiencies in the afterburners of these units are greater than 95 %. Decontaminated soil retains its physical properties. Unless being heated to the higher end of the LTTD temperature range, organic components in the soil are not damaged, which enables treated soil to retain the ability to support future biological activity.
Chemical oxidation converts hazardous contaminants to non-hazardous or less toxic compounds that are more stable, less mobile, and/or inert (García-Cubero et al., 2010). The oxidizing agents most commonly used in the treatment of contaminated soil are ozone, hydrogen peroxide, Fenton’s reagent, sodium persulphate, potassium permanganate (US EPA, 2004; ITRC, 2005; Mecozzi et al., 2006). Recently some studies have proved the effectiveness of chemical oxidation towards contaminated sediments characterised by a high content of fine grains, moisture and organic matter, and by the presence of different classes of organic pollutants (Ferrarese et al., 2008).
The authors are currently evaluating the efficaciousness of wet oxidation (WO), which, as known, is effective towards organic sludges (e.g. sludges produced in municipal wastewater treatment plants) and gives an inert final product. WO transforms the organic and inorganic substances through chemical oxidation (air or pure oxygen are used) and hydrolysis reactions (it is performed in an aqueous phase). The basic assumption is that the reactivity of oxygen, or its capacity to oxidize, increases with temperature. On the other hand it is necessary that the process occurs in the liquid phase, in order to support the oxygen contact with the organic matter. Therefore, in order to maintain both the conditions of high temperature and liquid phase, it is necessary to operate at high pressure. Operative temperatures range from 150 to 360 °C and running pressures are generally kept between 30 and 250 bar. Contact time is maintained in the range 15 - 120 min. During WO, the insoluble organic matter is turned in simple soluble organic compounds which subsequently are oxidized and may be converted into carbon dioxide and water. Effluent suspension can contain fatty acids with a low molecular weight, ammonia, inorganic acids and inorganic salts. The output gases can contain ammonia, CO and some low molecular weight compounds, in addition to CO_2, water steam and oxygen (Kolaczkowski et al., 1999; Debellefontaine and Foussard, 2000; Genç et al., 2002).

2. Materials and methods

The study was conducted in three steps. The first one was aimed at identifying normative constraints for the reuse of sludge originated in soil washing plants. Italian laws were analysed and experts in environmental regulations working in public bodies were consulted.
The second step was oriented to evaluate the practicable industrial alternatives for the sludge reuse and to define the technical constraints. An in-depth research and analysis of scientific papers and case studies was followed by semi-structured interviews with managers of industrial plants potentially

interested in receiving the sludge. The aim of the interviews was to define the desirable characteristics of the sludge in order to allow its reuse at reasonable costs.
The third step was carried out to assess TPHs removal from the sludge by WO. Lab-scale WO tests were carried out in a continuously stirred autoclave operated in batch mode (Figure 1), which was fed with an aqueous suspension containing the sludge produced in a soil washing pilot plant. The main characteristics of the reactor were the following: volume: 1.75 L; material: steel; maximum tolerable temperature: 350 °C; maximum tolerable pressure: 200 bar. The reactor was equipped with an electric heating jacket, an internal water cooling system to control reaction temperature, a system for pressure control and a mechanical stirrer.

Figure 1: Wet Oxidation reactor used in the experimentation.

The experimentation is still on-going. So far, tests have been carried out by varying the temperature between 150 and 300° C. Reaction time and initial oxygen pressure were fixed in 30 min and 20 atm, respectively. Further tests will be conducted by varying reaction time and initial oxygen pressure.
The suspension used in the experimentation was created adding distilled water to the sludge produced in a soil washing pilot plant in order to obtain a concentration of total solids (TSs) suitable for WO tests. The suspension was characterised before and after treatment by determining concentrations of TPHs, COD, and TSs.

3. Results and discussion

3.1 Normative constraints

The Italian legislation regulating waste recovery is the Legislative Decree 152/2006 (2006) and its subsequent amendments and additions. The law provides two different modalities for waste recovery: the simplified scheme and the ordinary scheme.
In the simplified scheme, waste can be recovered if it meets a set of standards (provided in a special ministerial decree) and recovery procedures, while formalities are limited to a "communication" to the competent authority. If only one of the requirements for the simplified scheme is not observed, waste recovery is still possible, but must be authorized by a special decree from the competent Authority (that is the ordinary scheme). In this case, specific ordinances are imposed by the Authority, in respect of the general waste legislation.
Waste hazardousness is one of the parameters to consider when deciding which scheme should be applied. Currently the major problem occurs when hazardousness is considered according to carcinogenicity: it is assigned depending on the concentration of hydrocarbons in the waste, but in Italy an official method of analysis has not been settled by the legislator. Therefore the situation is confused, since different methods, both at national and international levels are applied and concentration values are significantly different according to the principle used. Moreover many laboratories prefer to adopt proprietary methods or combinations of methods.

Concerning hydrocarbons, a soil is considered hazardous if the concentration of total hydrocarbons is greater than 1,000 mg/kg_{dw} and contains at least a polycyclic aromatic hydrocarbon classified by the EC as carcinogen of Category 1 or Category 2 in accordance with Annex 1 of the Council Directive 67/548/EEC (1967), with concentration higher than 0.001 mg/kg_{dw}.

3.2 Technical constraints

The sludge resulting from the soil washing process is, from the granulometric point of view, comparable with fine residues resulting from mining activities; it has, generally, a moisture between 20 % and 30 %, a particle size lower than 0.063 mm and a mineralogical composition essentially due to the rock it derives from (calcareous rocks, dolomite, porphyry, etc.).

Conventional uses of fine particles fall mainly in the civil construction field, e.g. in the production of bitumen-based binders (Hill et al., 2001), cement, concrete (Topçu and Urlu, 2003), or bricks. However, the use of silty materials in that field is limited by uncertainty about their physical properties and the effects they may have on different products (bricks, cement, bitumen, etc..). Silty material can be used also as a filling material of former quarries (Fraser and McBride, 2000) or as unbound aggregate, typically in road foundations (De Rezende and De Carvalho, 2003) or rail foundations (Touahamia et al., 2002), where it can be mixed with lime in order to improve its mechanical characteristics.

The use of raw sludge produced in soil washing plants implies a potential risk of environmental contamination, therefore, in any case, the basic condition for sludge recovery and reuse is its decontamination.

Technical managers of cement works that were interviewed affirmed that the reuse of uncontaminated sludge is technically and economically convenient if its moisture is inferior to 15 % because the higher the moisture, the higher the consumption of thermal energy and related costs. It means that sludge dewatering should be very effective and it should be verified if such a low percentage of moisture can be obtained with standard mechanical devices such as filter-presses. Moreover, organic matter should be as low as possible (however lower than 2 %) because very strict limits are usually imposed to cement works for volatile organic compounds (VOCs) in gaseous emissions.

Brick works do not need excessively dry materials because an adequate moisture favours their workability; anyway, the sludge coming from soil washing plants should not present moisture higher than 25 - 30 %. In order to guarantee suitable and constant characteristics of the final product, it is very important for brick works to receive homogeneous and substantial parcels of sludge with the same mineralogical characteristics. This is a strict constraint from the operational point of view because soil washing plants usually treat soils coming from different areas of the Italian territory; technical managers of those plants should organise soil treatment and storage according to its mineralogical characteristics.

The use of sludge mixed with lime as stabilised soil beneath roads is possible but sludge moisture should be about 20 % in order to favour its workability. Moreover, the total level of soluble sulphates in the sludge should be below 0.3 % to prevent the formation of ettringite and, as a consequence, very large volume increases, up to 250 %.

3.3 Decontamination of soil washing originated sludge by WO

TPHs concentration in the raw sludge was 14,300 mg/kg_{dw}. The aqueous suspension that fed into the reactor had the following characteristics: TSs = 20.8 %; TPHs = 2,950 mg/L; COD = 42,857 mg/L.

Figure 2 summarises the preliminary results of the experimentation: concentrations of TPHs in the suspension after treatment and related removal efficiencies are shown.

As expected, the higher the temperature, the higher the removal efficiency of TPHs. 57.9 % of removal efficiency was obtained at 150 °C of reaction temperature, increased to 63.0 % at 200 °C. A much higher efficiency, i.e. 94.8 %, was obtained at 250 °C, whereas at 300 °C the removal efficiency increased just a bit, reaching 98.0 %.

At the end of the test conducted at 250 °C, TSs were 20.0 %, so TPHs concentration referred to the dry material resulted equal to 745 mg/kg_{dw}.

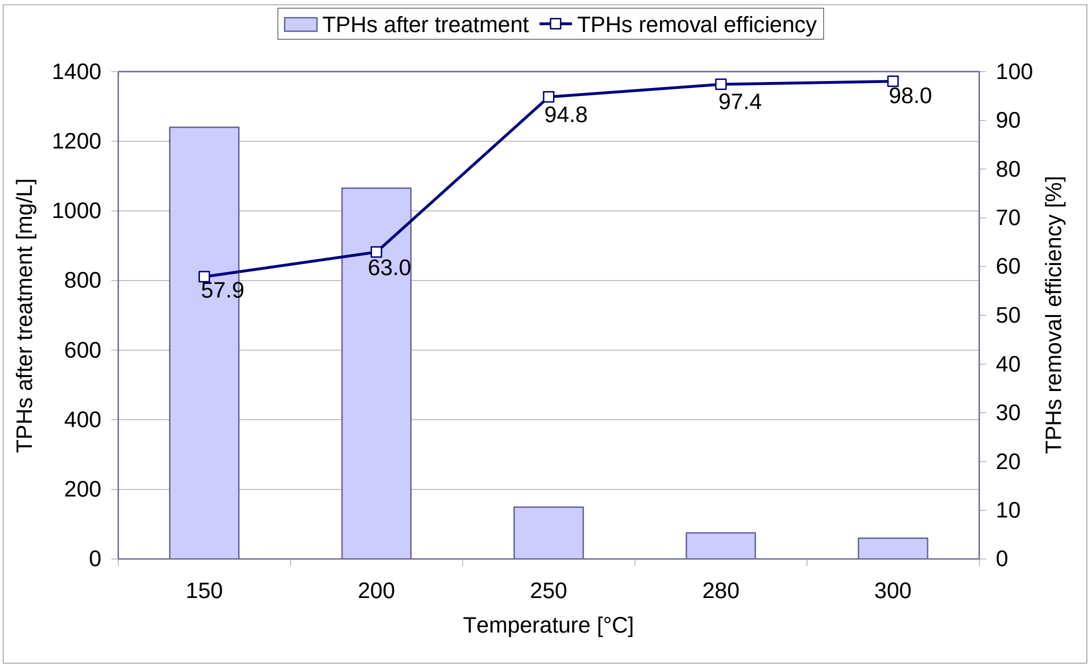

Figure 2: Concentration of TPHs after treatment and related removal efficiency.

4. Conclusions

Sludge landfilling weighs a lot on the operational costs of a soil washing plant. According to the authors' estimations, nowadays the cost for sludge landfilling in Italy varies between 15 and 35 €/t of contaminated soil treated in the plant.

The reuse and valorisation of soil washing originated sludge is desirable not only from the economic point of view but also because Italian and European legislation put waste recycling as a priority. Several tens of thousands of tons of sludge are produced and landfilled in Italy every year; they represent materials which could be exploited in place of virgin silt and clay to produce stabilised soil for road construction or bricks in brick works. Sludge reuse for cement production is possible, too, but it is probably more expensive.

The use of raw sludge produced in soil washing plants implies a potential risk of environmental contamination therefore in any case the basic condition for sludge recovery and reuse is its decontamination.

Sludge decontamination can be theoretically obtained by thermal desorption, solvent extraction or chemical oxidation. Wet oxidation tests executed by the authors indicate that such a process is potentially applicable. 98 % removal efficiency of TPHs was obtained in a lab-scale reactor setting temperature, treatment time and initial oxygen pressure to 250 °C, 30 min and 20 atm, respectively. Further tests will be carried out in order to identify the most favourable and cheapest treatment conditions.

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