Reclaiming Polluted Marine Sediments. A Case History

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Abstract — The Development Plan of Taranto port (S. Italy) predicts the dredging of approx. 20 Mt sediments, ≥10% of which are polluted. By appointment of Italian Environment Ministry, a detailed experimental investigation was carried out at laboratory and pilot-scale levels on the best available techniques to reclaim the polluted sediment so to reuse it in a technic and cost effective manner. A short pre-activation of sediment by mechanochemical technique followed by aerobic biodegradation offered most effective decontamination while the addition of cement with blast-furnace slag and coal fly ash allowed profitable reuse of the de(un)contaminated sediments.

Keywords—marine sediments; port pollution; PAHs; hydraulic additives; coal fly ash, waste reclamation and reuse.

I. INTRODUCTION

In order to ensure safe access to waterways and harbors, where 90% of total economic exchanges occurs today, 600 Mm³/y of sediments are dredged worldwide, 300 and 200 Mm³/y in USA and Europe respectively [1]. Although more stringent international regulations and conventions ensured significant progress in the reduction of marine pollution [2-7], 10-25% of dredged sediments are still contaminated and must be managed properly to avoid detrimental effects on port development [8].

Different national situations and socio-political interests prevented so far the achievement of a common position among developed countries, with USA long involved in national programs like Superfund (over 120 sediment sites already remedied or evaluated for cleanup) [9-11]. A regulatory framework for sediment risk and assessment able to intersect Waste/Water/Marine Strategy Directives was not agreed yet in the EU, where remedial decisions are still based on domestic standards and programs [12-18]. Following specific instruction by the Environment Ministry [19], Italy added a 4-color code (green, yellow, red, purple as the contamination level increases) to the European waste classification code EWC #170506 and 170505* for non-hazardous and hazardous sediments respectively. Unless properly remedied, accordingly, purple/red sediment must be costly destroyed or disposed of in special sanitary landfills while yellow/green sediment may be reused directly for maritime and other civil infrastructures.

Pollution by petroleum hydrocarbons is one of the major environmental problems in ports, mainly associated to heavy boat and ship traffic or to nearby industrial activity. Polycyclic Aromatic Hydrocarbons pose the greatest risk for human health and the environment after benzo[a]pyrene was listed among priority pollutants, certainly carcinogenic for humans [20]. This is the case, in particular, of Taranto port (S. Italy), among the busiest and closest Mediterranean industrial harbors to Suez channel trading route from Far East.

The new Development Plan recently approved for Taranto port commands dredging of ≈20 Mt overall sediments [21], approx.10% of which (the top layer made by brittle build-up) resulted polluted by PAHs (and, to a much lower extent, by Poly Chloride Biphenyls, PCBs, and few heavy metals) and was classified purple/red waste, so its destruction or disposal in special sanitary landfill requires huge amount of money [22].

As discussed in detail elsewhere [23], biological treatment of PAHs, PCBs and other persistent organics is cheap, but very slow, while its physicochemical degradation requires risky costly conditions so safer methods are still looked for.

On the other hand, major part of Taranto sediments (90%), classified yellow/green waste, made by silt/clay, needs excessive time to settle down naturally (≥500 years) before reaching the physical strength required to build upon piers or other planned maritime infrastructures. Accordingly, an experimental investigation was undertaken at laboratory and pilot scale levels, aimed at finding out most effective treatment(s) to achieve the decontamination and possible reuse of Taranto sediments by boosting their geotechnical consolidation. Based on the encouraging results obtained during previous investigation [24], special attention was paid to the use of mechanochemical pretreatment in order to activate polluted sediments.

Mechanochemistry is a well-known technique dealing with chemical reactions improved by the action of mechanical forces due to high temperature peaks (≥1,000°K) for extremely short time (10¹⁵sec) [25-26].
According to most acknowledged mechanochemical magma-plasma theory, the energetic outputs are responsible for the formation of a plasmatic state characterized by the emission of fairly excited fragments of solid substance, electrons and photons over a short time scale, which permit chemical reactions, otherwise extremely difficult, unfavorable and lengthy, to occur easily even at room temperature [27].

The paper summarizes the results obtained during the present investigation with Taranto sediments.

II. MATERIALS AND METHODS

Tab.1 and Fig.1 show the physico-chemical characteristics of the sediments dredged at 3 contaminated sites of Taranto port (hot spots A-B-C) [28].

<table>
<thead>
<tr>
<th>Parameters (mg/kg)</th>
<th>Samples A (non-hazardous)</th>
<th>Samples B (hazardous)</th>
<th>Samples C (non-hazardous)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silt (%)</td>
<td>20.6</td>
<td>20.6</td>
<td>20.6</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>14.4</td>
<td>10.3</td>
<td>14.4</td>
</tr>
<tr>
<td>Humidity (%)</td>
<td>48.1</td>
<td>48.1</td>
<td>48.2</td>
</tr>
<tr>
<td>pH</td>
<td>6.6±0.11</td>
<td>6.6±0.14</td>
<td>6.6±0.11</td>
</tr>
<tr>
<td>Organic matter</td>
<td>4.4×10^-3</td>
<td>4.4×10^-3</td>
<td>4.4×10^-3</td>
</tr>
<tr>
<td>BHC (Heavy Hydrocarbons, with C &gt; 12)</td>
<td>12.0±0.10</td>
<td>12.0±0.10</td>
<td>12.0±0.10</td>
</tr>
<tr>
<td>Total PCBs</td>
<td>0.05±0.03</td>
<td>0.05±0.03</td>
<td>0.05±0.03</td>
</tr>
<tr>
<td>Total PAHs</td>
<td>0.05±0.03</td>
<td>0.05±0.03</td>
<td>0.05±0.03</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>0.05±0.03</td>
<td>0.05±0.03</td>
<td>0.05±0.03</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>0.05±0.03</td>
<td>0.05±0.03</td>
<td>0.05±0.03</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>0.05±0.03</td>
<td>0.05±0.03</td>
<td>0.05±0.03</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>0.05±0.03</td>
<td>0.05±0.03</td>
<td>0.05±0.03</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.05±0.03</td>
<td>0.05±0.03</td>
<td>0.05±0.03</td>
</tr>
</tbody>
</table>

Laboratory tests for decontaminating polluted sediments

Sediment samples were activated mechanochemically using a high-energy (≤40 times ground acceleration, g) “nutation” mill (mod. Hicom 15 by FLSmidth, Brisbane, Australia) shown in Fig.2. To that aim the sediment was added with proprietary reagents and milled for ≤10 min under the operating conditions shown in Tab.2.
Among various treatments experimentally investigated at laboratory level (soil washing, stabilization/solidification etc.), most promising results were provided by the aerobic biologic degradation of mechanochemically pre-activated sediments.

The specific bacterium *N. pentaromativorans* is able to bio-degrade B[a]P along the pathway in Fig.3 [31-32], but a 15-years reaction time was extrapolated to achieve full B[a]P biodegradation in the optimum laboratory conditions investigated [23].

### Pilot-scale tests for reusing un(de)contaminated sediments

In order to cope with the 50 kPa carriage load required for reusing the sediment in new piers, 30kg of sediments were added with increasing amounts (6-10-15% w/w) of various hydraulic binders: lime; Portland cement with blast-furnace slag (CEMIIIA 32.5N); Composite cement with coal fly ash (CEM V/B S-V 32.5N); mixture by 30% CEM IIIA 32.5N cement+70% lime. After thorough mixing, the added sediment was allowed to cure for 28 days in sea water in a 5 m³ cylinder tank equipped with Ø 30 cm iron plate and probes for strength measurement at increasing pressure (≤1,000kPa) for 24 h.

### III. RESULTS AND DISCUSSION

Target contaminants (i.e., total and single PAHs, including B[a]P, HHCs. As etc.) in Taranto sediments showed higher concentration than in 2009 controls [19], indicating that port pollution still progresses. Exceeding the limits in force by the Italian waste regulation [30], the sediments are classified *hazardous* waste (EWC code 170505*) and require proper decontamination treatment in order to be reused for local maritime infrastructures like the yellow and green sediments.
Based on the experimental results, the following Michaelis Menten-type rate equation for the biodegradation of MC-activated PAHs was obtained (see Fig.5):

\[ V_{\text{biodeg}} = \frac{43 \times [\text{PAHs}]}{366 + [\text{PAHs}]} \]

with max degradation rate \( V = 43 \text{ mg/kg xd} \) and Michaelis Menten constant \( K = 366 \text{ mg/kg} \).

According to the \( V_{\text{max}} \) value, the biodegradation of the MC-activated PAHs (1,220 ± 580 mg/kg in Tab.1) should occur in approx. one month, as found experimentally.

Quite interesting, MC-activation (i.e., fast biodegradation) was most effective toward higher molecular weight PAHs, notoriously more resistant to biological degradation. This appears from Fig. 6, where PAHs are represented by their octanol/water partition coefficient, \( K_{\text{OW}} \). PAHs with larger \( K_{\text{OW}} \) (i.e., with higher affinity with the organic matter abundant at sediment surface) undergo greater degradation (≤90%) than those with small \( K_{\text{OW}} \) (50-80%): they are more involved in the formation of the plasma state at the solid particle edge, hence more prone to MC activation.

In fact, all contaminants underwent astonishing (90%) bio-degradation in few weeks.

Based on these results, a new process has been developed called BioMec®, allowing for easy biodegradation of waste contaminated by Persistent Organic Pollutants (POP) [33]. The economic evaluation of the BioMec® process (detail undisclosed) provided an overall cost (MC activation + bio-degradation including amortization) of 100€/t of sediment, i.e., approx. half the cost for its thermal destruction or for sanitary landfilling abroad.

As for the consolidation treatment to reuse the sediments for building new piers, all the additives investigated offered finite decrease of Plasticity Index in the Casagrande chart. As shown in Fig.7, the best results were achieved adding 10% w/w Portland cement with blast furnace slag (CEM IIIA 32.5N) or composite cement with 12.75% blast-furnace slag+2.25% coal fly ash (CEM V/B S-V 32.5N).

![Fig.4. Effect of MC activation on biodegradation of B[a]P (mg/L)](image)

![Fig.5. Biodegradation rate of mechanochemically activated PAHs](image)

![Fig.6. % biodegradation of MC-activated PAH as a function of K_{OW}](image)

![Fig.7. Type/amount of hydraulic additive vs. sediment characteristics](image)
Fig. 8 compares the strength stress resistance by addition of CEM IIIA 32.5N or by CEM V/B S-V 32.5N cement [34]: performance of the former was better, although the latter (partial substitution by fly ash) was noticeable too.

Finally, Fig.9 shows the results of compression tests with stepwise increase of load pressure: after 24h at the target load of 50 kPa, pressure was progressively increased until the ultimate tensile stress of the added sediment occurred.

It can be seen that the sediment added with 15% of Composite cement (CEM V/B S-V 32.5N) showed a 0.67 cm failure and its breakdown started only at ≥800 kPa load.

IV. CONCLUSIONS

Experimental investigation carried out with polluted marine sediments (EWC 170505*) of Taranto port indicated that proper pre-activation by the mechanochemistry technique allows to obtain the complete biodegradation of persistent contaminants like PAH and HHC in weeks instead of years.

Furthermore, by proper addition of cement prepared with other waste, i.e., Portland cement mixed with blast-furnace slag (EWC 100202) or with coal fly ash (EWC 100102), the silty-sandy sediment rapidly achieved the geotechnical characteristics necessary to cope with the 50 kPa carriage load required to build upon new piers or similar civil infrastructures.

REFERENCES

[22] www.port.taranto.it