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INNOVATIVE REMEDIATION AND MONITORING SYSTEM INSIDE AN AREA USED FOR PAPER SLUDGE RECOVERY

NOUVEAU SYSTÈME D'ASSAINISSEMENT ET DE SURVEILLANCE D'UN SITE UTILISÉ POUR LA RESTAURATION AVEC DES BOUES DE FABRICATION DU PAPIER

INNOVATIVO SISTEMA DI BONIFICA E MONITORAGGIO DI UNA AREA UTILIZZATA PER IL RECUPERO DI FANGHI DI CARTIERA

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Abstract

An innovative bioremediation technology and strategy were applied to a former-quarry area in Imola (BO – Italy) concerned by an incorrect environmental restoration of paper sludge, with subsequent uncontrolled biogas production and migration to the adjacent area. An Emergency Plan was implemented by the isolation of the buried sludge area and a characterization project was performed to define an appropriate permanently safe recovery. An innovative biological *in situ* treatment, avoiding paper sludge removal, was adopted; it was based on the use of tailored compost and enzymes to reduce methane production and concentration. This was integrated by specific monitoring piezometers for both biogas (CH_4, CO_2) and oxygen monthly measurements, and also the application of a respirometric technique application to buried sludge for assessing its stabilisation under aerobic and anaerobic conditions. This communication describes the strategy used, the treatment and monitoring system and the results of 3 years field pilot application. Monitoring work is still in progress.

Keywords: *methane; explosion; environmental restoration; paper sludge; tailored compost*

Résumé

Ce document décrit une technologie (bio) d'assainissement et une stratégie novatrice appliquée à une zone d'ancienne carrière à Imola (Bologne - Italie), contenant des boues de papeterie et affectée par une incorrecte restauration de l'environnement; par conséquent est apparue une production incontrôlée de biogaz avec une migration ultérieure dans la zone adjacente. Un Mise en Sécurité d'Urgence a été appliquée, suivie d'un projet de définition d'une récupération permanente. Un traitement novateur biologique in situ, basé sur l'utilisation de "*tailored compost*" et d'enzymes a été réalisé dans le but de réduire la

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production et la concentration de méthane sans enlèvement des boues. Le traitement a été complété par un système de surveillance spéciale: grâce à des piézomètres pour mesurer mensuellement le biogaz (CH_4, CO_2) et l'oxygène, avec aussi une mesure de la stabilité profonde de la boue en conditions aérobie et anaérobie par des techniques de respirométrie. La communication décrit la stratégie utilisée, les systèmes de traitement et de contrôle, ainsi que les résultats des trois premières années de l'intervention pilote.
Mots clés: *méthane;explosion; restauration de l'environnement; boues de papeterie; "tailored compost"*

Riassunto

Una innovative tecnologia di (bio)bonifica è stata applicata ad una area di ex-cava in Imola (BO, Italia), oggetto di ripristino ambientale non corretto con fanghi di cartiera, dove si è prodotto biogas con migrazione nell'area adiacente. E' stato effettuato l'intervento di Messa in Sicurezza di Emergenza, seguito da un progetto di caratterizzazione per definire un appropriato recupero permanente. E' stato realizzato un trattamento biologico innovativo in *situ*, evitando la rimozione dei fanghi, basato sull'utilizzo di *tailored* compost e di enzimi, per ridurre concentrazione e produzione di metano. Il trattamento è stato integrato da uno specifico sistema di monitoraggio: piezometri per misure di biogas (CH_4, CO_2) e ossigeno, programma di misura mensile, applicazione di tecniche respirometriche per la stabilità in condizioni aerobiche ed anaerobiche del fango tombato. Il lavoro descrive la strategia utilizzata, i sistemi di trattamento e monitoraggio nonché i risultati dei primi 3 anni di intervento pilota.
Parole chiave: *metano; esplosione; ripristino ambientale; fango di cartiera; compost specializzato*

Introduction

This paper describes an innovative bioremediation technology and strategy applied to an ex-quarry area in Imola (BO – Italy), interested by a not correct environmental restoration with paper sludge, with subsequent uncontrolled biogas production and migration to the adjacent area.
The site, an ex quarry area for clay materials of about 49.000 m^2, in an agricultural zone, had been restored according to directive 91/156/CE (substituted by Dir. 2006/12/CE), in particular according to D.M. 5.2.98 (R10 be recovered spreading on land resulting in benefit to agriculture or ecological improvement). Different kinds of paper sludge were used such as: paper sludge, paper residue sludge, paper residue sludge, granulates, clarifier sludge and de-inking sludge for a total amount of 60.000 t; they were mixed with soil and then covered with a 2 m clay layer. Paper sludge are mainly composed by cellulose, hemicelluloses and lignin (Modarelli, 2008). Recovered sludge had been interested by anaerobic degradation with biogas (methane) production, favored by clay materials, which diffused throug permeable soil layers.
In December 2005, one year later the end of restoration efforts, biogas (methane) production and migration caused two explosions in a joint inside a building set in

an adjacent area (Dall'Ara et al., 2008). In the scientific references there are many case studies related to control of biogas production connected to buried waste (mainly landfills) and to bioremediation in site with organic contamination (mainly hydrocarbons) but there are no case studies similar to this one. In the meanwhile, explosions in building interspaces close to the old landfills are reported (Agency for Toxic Substances and Disease Registry). Furthermore methane is not considered as a contaminant (DM n. 471/99 e D.lgs n. 152/2006). Therefore Local Authorities (Municipality, Regional Agency for Environment Protection and Health Prevention, Local Sanitary Agency) had to face a new environmental emergency, without references for technical and administrative aspects.

At first, an emergency safety plan was set up to assure safety condition for inhabitants and buildings in the site adjacent area: a perimetric trench, 7 meters deep, to intercept biogas migration towards targets and a soil vapour extraction system around the site and to extract biogas. In the meanwhile, preliminary tests were performed in order to select a proper technology for inside site reclamation to remove biogas and to undo its production. In fact, in this peculiar situation, reclamation efficiency is connected to: i) reduction of methane production (generative term); ii) reduction of methane concentration.

Paper sludge, known as stable material, are considered stabilized organic wastes. Preliminary characterizations have underlined that paper sludge are "very stable" organic matter in aerobic conditions with Potential Dynamic Respiration Index values below 500 [mgO_2/(kg SV*h)-1] (Adani F., 2004; Adani F., Confalonieri R. & al., 2004). Otherwise in anaerobic conditions the same substance resulted "potentially reactive" with Biochemical Methane Potential values at 100 days in some cases above 78 [CH_4 Nm^3/t_{TS}], values that are a little lower than the ones typical of undifferentiated Municipal Wastes (Bonoli et al., 2008; Grilli et al., 2008). The chemical-physical characterization of buried sludge before treatment is reported in Dall'Ara et al (2008); samples showed a high water content (up to 60%), a high volatile component and a C/N ratio higher than 100, typical of sludge and not of soil.

The objective of this work is to describe the strategy used, the treatment and monitoring system adopted for site reclamation and the results of 3 years field pilot application.

The first step was the definition of a proper bioremediation technology to reach permanent safe conditions. Different technologies were applicable at the beginning of 2006. Site physical and chemical characteristics were very variable in term of mixing ratio sludge/soil, permeability, presence of suspended water table and biogas concentration as showed by initial geophysical investigations; therefore choice of proper technologies was restricted to the following ones: i) Sludge mixed with soil removal and subsequent treatment/disposal in authorized plant (landfills); ii) Bioventing; iii) Biopile on site, and sludge mixed with soil removal (Dall'Ara *et al*., 2009).

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The first solution, the removal of 60.000 t of buried sludge with at least 120.000 t of mixed soil, would have requested 5 years and unacceptable environmental (noise, odour, dusty) and economic costs. Also the other solution had environmental drawbacks. An innovative biological technique was employed for in *situ* biostabilisation treatment, based on the use of tailored compost and enzymes to reduce methane production and concentration, according to a patent pending process (Amek, 2008), without sludge removal. The bioremediation project was proposed by APICE srl (Imola, Bo, Italy) as coordinator of site reclamation, project based on AMEK (Fe, Italy) technology and know-how.

Materials and methods

For the area safety intervention it was adopted a bioremediation treatment consisting in: i) an in *situ* biostabilisation treatment using compost designed and vegetal enzymatic mixtures to reduce the methane production and concentration; ii) well monitoring to measure biogas (CH_4 e CO_2) and oxygen concentration; with monthly monitoring Gas Analysis Program iii) utilization of innovative respirometric laboratory techniques to check potential methane production and sludge stability under anaerobic conditions by means of Biochemical Methane Potential (hereafter BMP) (Marroni *et al.*, 2006, Bonoli *et al*., 2008).

In situ biostabilisation treatment

The technique is site and sludge specific and oriented to site recovery for agricultural activities; it is in *situ* biostabilisation treatment based on the use of tailored compost, rich in cellulosolithic microorganisms, and enzymes to reduce methane production and concentration, according to a patent pending process (Amek, 2008). Biostabilisation treatment was performed creating physical discontinuity introducing special compost with lower density and designing biogas preferential pathways by passive convection. Two kinds of opencut have been used: biofilter and biopile. Biofilters, filled with designed compost and enzyme mixture, can be used as preferred pathways for biogas draining and transport towards atmosphere and contemporary methane bioconversion to CO_2 by tailored compost. Biopile opencut is obtained by mixing designed compost, enzymes and the extracted sludge. Biofilters have a function similar to "bio windows" proposed by Kjeldsen *et al*., (2009) for old landfill biocover to obtain methane bioconversion to reduce greenhouse gas emissions.

Biogas monitoring

The gas phase was monitored in 21 wells inside the perimeter investigated to measure indirectly the microbial metabolism and its modifications. The gas concentration was measured in situ and it's the result of production, accumulation and dispersion of gas throughout the area (Modarelli, 2008). CH_4, CO_2 and O_2 concentrations were measured using a portable instrument (GA 2000 PLUS, Geotechnical, UK). Methane is the main indicator of the dangerousness of biogas; its relationship with CO_2 concentration can verify changes in fermentation processes. The relation oxygen and methane concentration is an indicator for hazardous conditions and for changes within the fermentation processes.

The gas monitoring was carried out under equilibrium conditions, after piezometric level measurement and water pumping from the well. Gas concentration was measured in each well until a constant value (about in 300 s). Gas phase in the site has been monitored monthly.

Biogas Modelling

Stechiometric model was used to calculate the maximum amount of methane and biogas in the site; the main parameters used are reported in Table 1 (Modarelli, 2008), taking into account a 1:1 ratio for CH_4/CO_2.

Initial deposit year	2003
Organic matter (SV %)	22.5 (%)
Total Organic Carbon in sludge	88.8 (kg/t paper sludge)
Degradable substance Sd	80 %
Paper sludge amount	60,000 t

Table 1

Data used for methane and biogas production assessment.

To foresee biogas production along time (source term) and theoretical expected biomass evolution without intervention and to compare with experimental data, source term has been calculated by "Landfill Gas Emission Model" (LandGEM, http://www.epa.gov). The software, developed for landfill application, can calculate theoric landfill gas production along time, assessing also methane and carbon dioxide production. The model was implemented to the restoration site and the main input data are reported in Table 1, where it is evidenced that restoration had been performed in 2003 and 2004. Methane rate k value is similar to default figure (0.05) but it is specific for paper sludge (Salvatore, 2008); for initial Lo (biogas potential production) experimental BMP at 100 days data was adopted (Grilli *et al.*, 2008).

Parameters	Adopted values
Waste acceptance rates	20.000 Mg in 2003 40.000 Mg in 2004
Methane rate k (y^{-1})	0.046
Methane potential Lo (m^3/Mg)	40.5
Methane concentration (% v/v)	50

Table 2

Input Parameters used for Landgem model adopted for specific restoration site.

Solid phase sampling and characterization

The sampling plan was aimed at initial characterization for pilot field treatment, evaluating recovered material, operating and previous characterization. Initial characterization was used as reference for monitoring time evolution of sludge during treatment in the pilot area. Data were referred to dry matter and volatile substances when suitable, to overcome the effects of different degrees of mixing

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with soil. Representative solid phase samples were taken from the site by Geoprobe system. The sampling of the soil/sludge mixture was performed by direct push soil probing techniques. The samples were collected by slotted PVC well screen pipe (ID 1 in. and 1.20 m long) surrounded by a stainless steel mesh. In this way we had minimal disturbance of natural formation conditions (Figure 1). For respirometric measures large quantities of sludge were taken by means of a bucket.

Figure 1

Example of soil/sludge mixture sample

Respirometric laboratory tests such as Potential Dynamic Respirometric Index (hereafter, DRI) and Biochemical Methane Potential (hereafter, BMP) were used to estimate aerobic and anaerobic sludge biodegradability as well as short and long time potential impacts (Grilli et al., 2008). The DRI [mgO2 KgVS-1 h-1]) was used as the reference index for the determinations of the aerobic biological stability in according to the European method UNI/TS 11184 (Technical Specification) adopting the Costech Instrument 3022 Respirometer and the test duration was protracted to four days more (lag phase + 4 days), in according to Binner E.(2003). The initial wet weight of samples collected from plant ranged from 20 to 30 kg. The sampling and the respirometric test procedures were carried out in according to the European method UNI/TS 11184 Technical Specification. All samples were tested in duplicate and previous standardization of the moisture content and pH (potential DRI). The anaerobic tests for the determination of BMP (Nm3CH4/t VS) over 30 and 100 days were performed in batch conditions, using pyrex glass bottles with of 500 mL capacity as reactor (Environment Agency England and Wales, 2005; Trine et al., 2004).

Results and discussion

Biostabilization Pilot Application

Permanent safe recovery has been performed in three different phases from June 2006 to November 2007 (Modarelli, 2008); at first a pilot area of 130 m2, then a pilot treatment of 70% of site area completed by September 2006 and finally the extension to the whole area. The dumping work was completed before June 2007.

The surface and sub-surface hydrogeological water arrangements were completed by September 2007, avoiding interference with the freatic aquifer. Finally a green cover was performed in order to reduce the water collection inside the area (Bonoli et al, 2008). An aerial view of the site after bioremediation pilot application is reported in Figure 2.

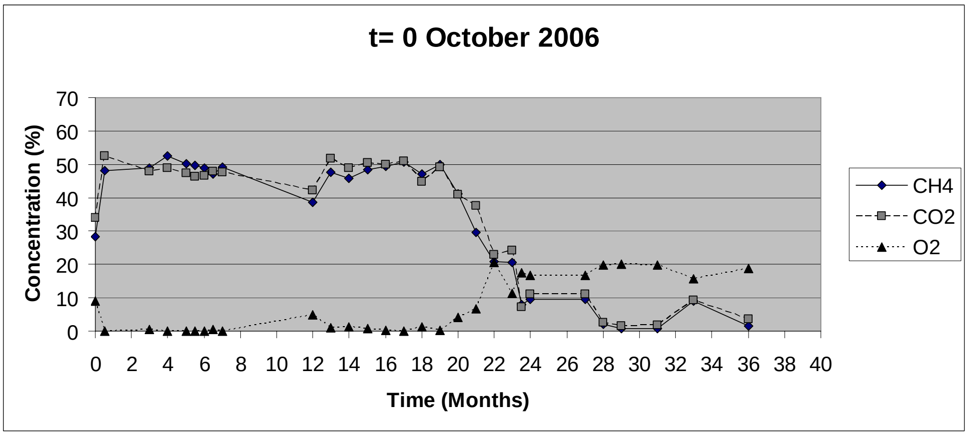
Figure 2

Aerial view of the site after bioremediation pilot application

Biogas monitoring

The results of the first 36 month gas monitoring are reported in Figure 3, which shows the typical trend along time of CH_4, CO_2 and O_2 concentration. At the moment, graphics show different phases: a first 20-24 months phase, during which

Figure 3 - *CH_4, CO_2 and O_2 concentration typical trend in a monitoring well; the bioremediation was completed at 12^{th} month, by October 2007.*



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system maintains high concentration; a second 4-6 months with methane concentration substantial decrease, and a third phase where the CH_4/O_2 ratio reaches a value < 1. As the bioremediation intervention was completed by month 12, the effect took place after 10-12 the treatment completion.
CH_4/CO_2 ratio was proximal to 1 during all monitoring period.

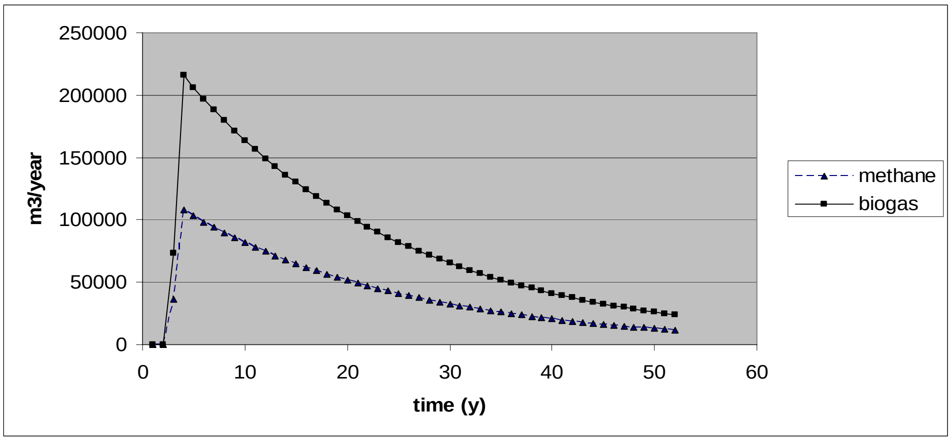
Solid phase characterization

BMP tests have not shown long lag phases, to indicate that the sludge is very reactive as soon as anaerobic conditions appear. Furthermore, more than 80% of the total production (178-183 CH4 Nm3/t VS) is reached within the first 30 days (BMP30), showing a fermentescible sludge under anaerobic laboratory conditions. Therefore, in anaerobic conditions, the same substance was "potentially reactive" with BMP values at 100 days in some cases above 78 [CH4 Nm^3/tTS], values that are a little lower than the ones typical of undifferentiated Municipal Wastes. (178-183 CH4 Nm^3/t VS).
After 14th treatment month, the methane production of the inside opencuts samples decreased and the BMP final values showed a significant decrease to 70 and 40 (Nm^3 CH4 /ton VS), respectively in different opencuts. In both monitored opencuts the methane production potential was reduced by more than 60%.
Instead, after the same treatment time the methane production of the outside open-cuts samples was about of 104 and 133 (Nm^3CH_4 tonVS-1) leading to a nearly 25% reduction of the methanogenic activity (Grilli *et al.*, 2008).

Biogas Modelling

The results of stechiometric model calculation is a specific mass or volumetric production for methane of 47 kg CH_4/t sludge or 66 Nm^3 CH_4/t paper sludge; these data are an overestimation of experimental 40,5 Nm^3 CH_4/t obtained via BMP measure, probably connected to.
Graph in figure 4 shows typical biogas production trend along time, calculated with LANDGEM model for the studied site.

Figure 4 - *Biogas and methane production along time calculated with Landgem model.*



A first growing phase is evident, with maximum in 2005, when biogas migrated and caused deflagration outside the site; this is followed by a decreasing phase, with exhausting in more than 30 years in the future, as showed by the trend of specific annual methane production.
These generative term would cause a continuous growing in methane concentration
A Chronogram of all events, from environmental restoration, is reported in Figure 5.

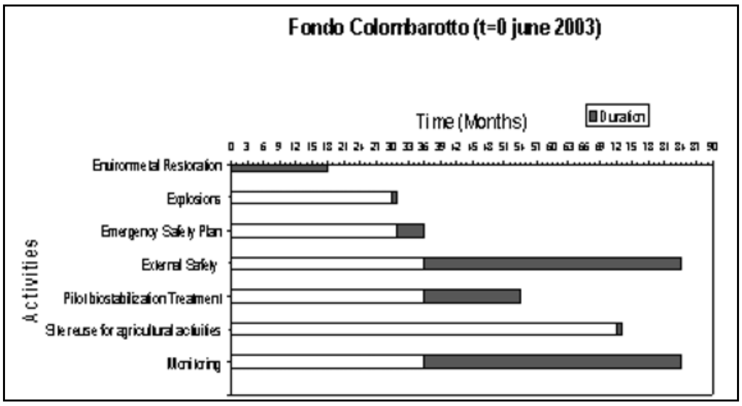


Figure 5

Chronogram of activities

Conclusions

An innovative in situ bioremediation method has been implemented in a restoration site interested by biogas production, to reduce methane concentration and production and for agricultural site recovery. A procedure step by step was adopted for the site application of a new technique.
The main feature of actual situation (4,5 years after deflagrations) are:

- Post intervention monitoring in progress,
- Site again in use for agricultural activities,
- Costs much lower in comparison with sludge mixed with soil removal.

Furthermore, the main predictable environmental and economic advantages for the biological technique have been verified:
- minimized acoustic impact and emissions into the atmosphere;
- reduced visual impact at the end of in-site operations (Figure 2);
- mitigated greenhouse gases effects;
- reduced operational costs;
-accelerated recovery to agriculture activities.
This case experience could give a bioremediation method applicable to other restoration sites, in agricultural areas, close to farmhouses and dwellings.

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