Asian Journal of Chemistry Vol. 21, No. 4 (2009), 2989-3000

Biodegradation of Iso-valeric Acid in Relation to Other Chemical Indexes and Spatial Liner Risk Assessment at Landfill Topographies - Mid Auchencarroch Experimental Site

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This paper analyses the effects of different waste management techniques and waste pretreatment on iso-valeric acid emissions and landfill mass biodegradation stages. The biodegradation of Mid Auchencarroch experimental landfill project is studied in 4 different cells. The variations of the examining experimental landfill chemical emissions and their spatial behaviour are presented and analyzed in order to take the right measures in time. The experimental Mid Auchencarroch's data confirm that leachate recirculation, waste pretreatment and co-disposal with inert material are sustainable, accelerating the waste biodegradation. An analysis is made for proper landfills' spatial monitoring and functional support measures so as to avoid any associated landfill emissions' risks and threats to public health.

Key Words: Landfill biotechnology, Leachates' organic acids, Solid waste biodegradation, Landfill spatial chemical analysis, Solid waste chemical emissions, Experimental landfill design.

INTRODUCTION

Undoubtedly, sanitary landfill controlled method will remain as an attractive economic disposal method for solid wastes, not only because it is necessary to adopt any remnant waste material by other waste treatment methods, but also it provides better opportunities for environmental impacts' minimization, potential hazard control and an increasing potential for resources' recovery.

Landfill biodegradation processes are complex, including many factors that control the progression of the waste mass to final stage quality[1-7]. Leachate recirculation can provide an efficient sustainable management of landfill sites generating considerable volumes of methane gas, which can be exploited by landfill gas recovery installations to produce either electricity or to supply bio-fuels. Leachate treatment units should work properly in a sustainable way for water supply in irrigations networks and associated regional development public water works.

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The landfill gas and leachate generation is an inevitable result of the solid waste biodegradation in landfills and their study is necessary for future efficient designs, controlling air, soil and groundwater pollution[2,8,9]. The use of controlled landfill projects is necessary for quick site stabilization of landfill gas and leachate emissions, avoiding any long term emissions to the environment. Proper spatial numerical models, digital databases should be used for the right lining of monitoring boreholes, having a better landfills' emissions spatial control, avoiding any spatial associated environmental impacts to flora, fauna and public health and taking any probable necessary reclamation, bioremediation works taking into account the surrounding topographical characteristics adjacent to landfill boundaries[9-12]. Moreover, the use of controlled batch anaerobic bioreactors accelerates waste biodegradation in short periods, minimizing any associated environmental risks due to landfill emissions[8,9,13,14]. Any uncontrolled dumps have to close so as to avoid any threats to the public health and to protect the environment.

EXPERIMENTAL

The long term behaviour of Mid Auchencarroch experimental landfill site is assessed, based on particular landfill biodegradation parameters, making useful associated conclusions. The experimental landfill Mid Auchencarroch, which is located in Scotland, is a field scale facility, constructed in order to assess a number of techniques that promote sustainable landfill. Mid Auchencarroch (MACH) experimental landfill, has been an Environment Agency, D.T.I. and industry funded research facility. The project consists of 4 cells each of nominal volume 4,200 m^3. It has been capped since November 1995. The experimental variables are waste pretreatment, leachate recirculation and co-disposal with inert material with different disposed waste input materials into each cell[4,5,9,15].

The batch wet-flushing bioreactor landfill model attempts to develop and assess techniques to enhance the biodegradation and pollutant removal processes for municipal solid waste (MSW) landfill, achieving the goal of sustainability. In cells 1, 2 and 3 there is recirculation of leachate and in cells 2, 4 the disposed waste is untreated. In cells 1 and 3 there is pretreatment by wet pulverization and in cell 1 there is addition of inert material 20 % by volume. The MACH leachate and landfill gas data, which were used for the present paper, cover simultaneously the 22 month period of waste biodegradation at MACH site[9,15].

RESULTS AND DISCUSSION

Analyzing the MACH landfill gas emissions, it has been found that the peak landfill gas production, heat generation after 1996 at MACH site and the progressive reduction of methane, carbon dioxide (vol %) concentration in time, verify that methanogenesis biodegradation stage and quick site stabilization has been achieved in time[5,9]. The leachate concentration parameters change with waste input materials, landfill age and landfill conditions in time. Proper landfill leachates' collection and

treatment is needed so as not only to avoid any environmental impacts but also to exploit any resources, like valeric acid, which is an useful raw material for variety of industrial target compounds. Valeric acid is a member of the series of fatty acids of colourless liquid with a penetrating aroma, slightly soluble in water, soluble in alcohol and ether and boils at 185 ºC. It is used in flavourings, perfumes, plasticizers and pharmaceuticals. This compound reacts with bases, oxidizing agents and reducing agents. All the MACH cells were stabilized in short time period according to the experimental results of acetic acid, iso-butyric acid, TOC, BOD and COD, leachate emissions[4,5]. This paper analyzes characteristic leachate iso-valeric organic acid concentrations and trends, which were monitored at MACH experimental site, making useful conclusions.

The landfill biomass biological biodegradation includes the next stages *i.e.*, initial biological decomposition under aerobic conditions; hydrolysis stage takes place, where proteins are decomposed to amino acids, hydrocarbons are decomposed to sugars and fats to polyalcohol and fatty acids; production of organic acids stage, volatile fatty acids (VFA), where one of the most characteristic one in this stage of acidogenesis is the iso-valeric acid; stage of acetogenesis, where there is a peak production of organic acetic acid; methanogenesis stage and final maturation of landfill biological biodegradation. The main characteristic organic acids' concentrations, which can be used for the evaluation of biomass biodegradation, in landfill leachates except the iso-butyric acid and acetic acid is also the iso-valeric acid. Their measurements can be used for the landfill emissions' spatial monitoring of acidogenesis and acetogenesis stages, respectively and the lining of any related technical works to control proper. The concentration variation of the latter acids in time determines the landfill biomass biodegradation stages[7,9]. A combination of all the measurements of any available landfill emissions should be made so as to realize efficient risk assessments in the case that there is migration of landfill emissions to surrounded topographies next to landfill boundaries. In the latter case proper dynamic lining methods should be used and to take place on a given landfill topography for the right spatial confrontation[10-12].

Below, is evaluated the landfill biodegradation rate, based on the MACH site experimental field data, according to the above mentioned most characteristic biodegradation organic acids of the produced leachate emissions. Figs. 1-4 presented the iso-valeric acid concentrations and their trends in time, in the leachate emissions of MACH cells, in 22 month period since waste mass has been disposed into the landfill.

Moreover, Figs. 5-8 presented the biodegradation rates of chemical oxygen demand (COD), biochemical oxygen demand (BOD), acetic acid concentrations and pH values in leachate emissions of MACH cells, for the same time period as in the above figures, in 22 month period since waste mass has been disposed into the landfill. Chemical oxygen demand could be characterized one of the most hazardous toxic leachate characteristic chemical index in relation to groundwater and spatial

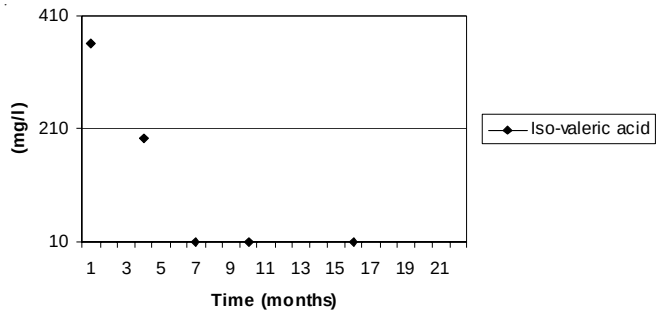

Fig. 1. Mid Auchencarroch's iso-valeric acid concentrations *vs.* time for cell 1

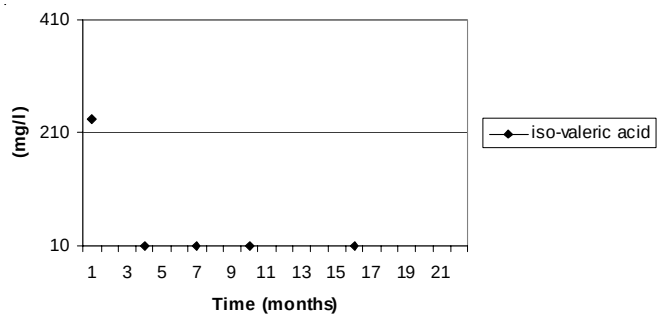

Fig. 2. Mid Auchencarroch's iso-valeric acid concentrations *vs.* time for cell 2

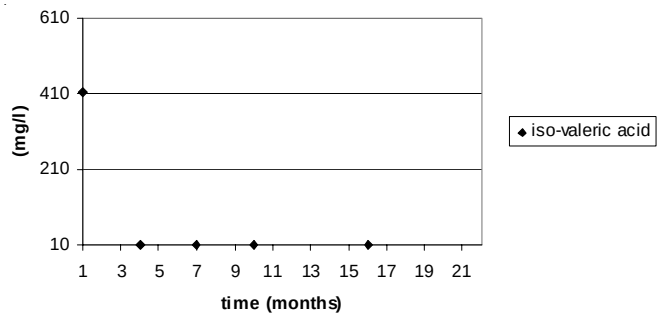

Fig. 3. Mid Auchencarroch's iso-valeric acid concentrations *vs.* time for cell 3

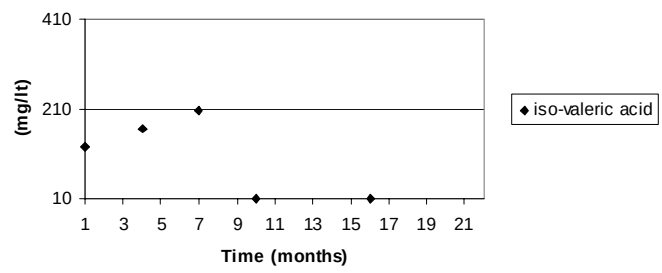

Fig. 4. Mid Auchencarroch iso-valeric acid concentrations *vs.* time for cell 4

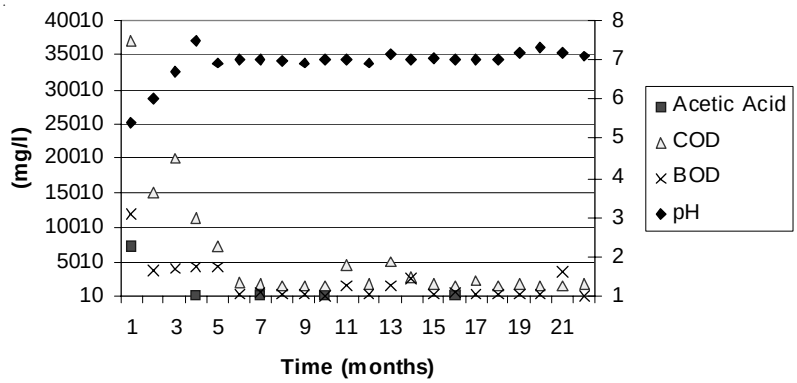

Fig. 5. Mid Auchencarroch's BOD, COD, acetic acid concentrations and pH values *vs.* time for cell 1

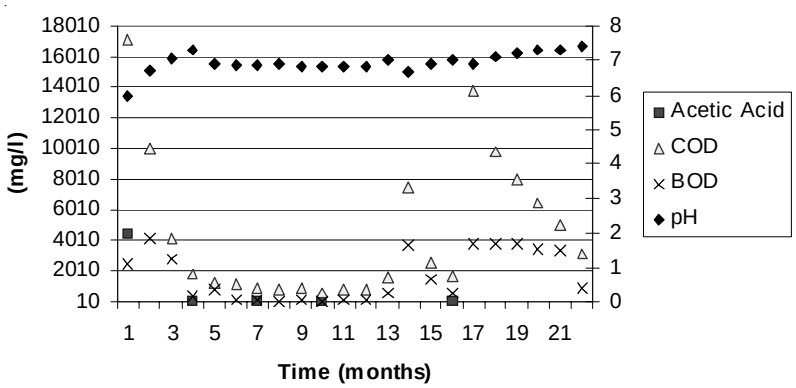

Fig. 6. Mid Auchencarroch's BOD, COD, acetic acid concentrations and pH values *vs.* time for cell 2

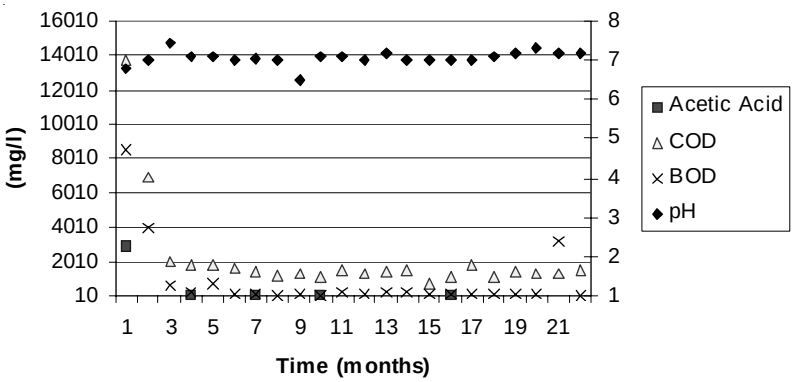

Fig. 7. Mid Auchencarroch's BOD, COD, acetic acid concentrations and pH values *vs.* time for cell 3

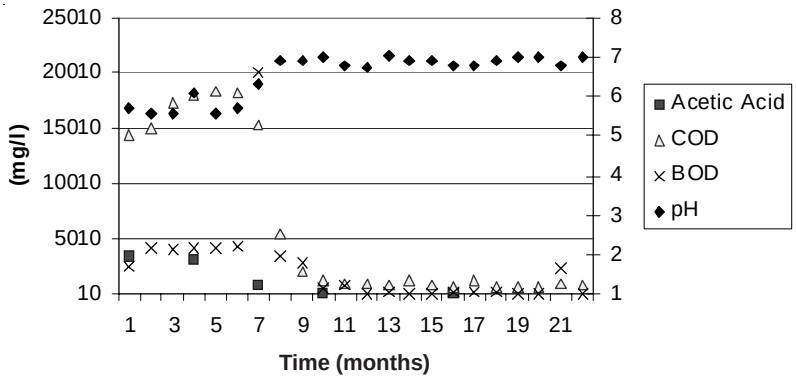

Fig. 8. Mid Auchencarroch's BOD, COD, acetic acid concentrations and pH values *vs.* time for cell 4

contamination from a landfill source, where proper lining of reclamation, bioremediation works should take place on a given topography for the right confrontation of any migrated landfill emissions[7,9-12].

The field data of the above Figs. 1-8 are analyzed in the next Tables 1-3 for BOD, pH and iso-valeric acid, presenting the maximum, minimum and average magnitudes of the respective chemical concentrations (mg/L) and pH values, respectively for each MACH experimental cell. All the above investigated chemical indexes for each MACH cell showed the following biodegradation trends, verifying that MACH's emissions stabilized efficiently in short time. However, the initial biodegradation trends of the examining chemical indexes vary due to the different waste inputs that have been disposed into MACH cells.

TABLE-1
MAGNITUDES OF BOD CONCENTRATIONS AT MACH EXPERIMENTAL CELLS

MACH cell	BOD max (mg/L)	BOD min (mg/L)	BOD average (mg/L)	Pretreated waste by wet pulverization
Cell 1	11850	55	1843.6360	Yes
Cell 2	4150	25	1659.0910	No
Cell 3	8500	15	857.1591	Yes
Cell 4	20000	15	2452.3860	No

TABLE-2
LEACHATES' pH VALUES AND LANDFILL GAS PRODUCTION RATE AT MACH EXPERIMENTAL CELLS

MACH cell	pH max	pH min	pH average	Landfill gas production rate (m^3 gas/t waste)
Cell 1	7.50	5.4	6.9	33.1
Cell 2	7.40	6.0	6.9	37.8
Cell 3	7.45	6.5	7.1	32.8
Cell 4	7.05	5.6	6.6	36.1

TABLE-3
MAGNITUDES OF ISO-VALERIC ACID CONCENTRATIONS AT MACH EXPERIMENTAL CELLS

MACH cell	Iso-valeric acid max (mg/L)	Iso-valeric acid min (mg/L)	Iso-valeric acid average (mg/L)	Leachate recirculation
Cell 1	360	10	136	Yes
Cell 2	235	10	55	Yes
Cell 3	415	10	91	Yes
Cell 4	205	10	103	No

According to the above experimental results of COD, BOD, pH, acetic acid and iso-valeric acid concentrations, are verified that there was a great depletion of carbon at MACH experimental cell 1 and cell 3. The experimental cell 2 presents temporarily high risk in the examining leachates' COD, BOD concentrations between the 15th and 21st month due to the fact that leachate recirculation began in November 1996. Moreover, MACH experimental cell 3 presents higher initial iso-valeric acid concentration in time than the rest ones due to the fact that there has been disposed pulverized wet treated biodegradable waste fraction content into it, verifying that organic depletion took place in short time. Moreover, the relative low pH values after 1996, for both cells, verify that the stages of acidogenesis and acetogenesis took place in short time period respectively, avoiding any long term chemical pollutant threats to the public health and to the environment.

According to the above presented experimental field data, the magnitudes of iso-valeric acid concentrations have reached low values in the first months for cell 1, 2 and 3. The latter fact verifies that acidogenesis biodegradation stage was integrated in short time period. In cell 4 there were found higher long term iso-valeric concentrations than the rest ones, in the first 8 months due to the fact that there has been disposed a higher untreated waste fraction of biodegradable carbon content, without any leachate recirculation, into it than at the rest cells. However, according to the above field data, we can see that the COD and acetic acid leachate emissions follow the same trends in time, verifying that the acetogenesis stage was integrated between the first 8 and 11 months for all MACH cells. As acetogenesis has been achieved, the methanogenesis stage is followed providing satisfactory landfill gas production according to the field date and the presented results of Table-2 (neutral pH has been achieved in short time period and satisfied landfill gas production rates have also been realized). The latter facts verify that an efficiently quick site stabilization at MACH experimental cells avoiding any long term chemical risks and hazards.

Risk assessment: The use of field data, utilization of collected data into digital databases and lining properly monitoring networks are necessary for the right control of landfill emissions and the development of risk assessment numerical models for further analysis of taking any relative security measures and bioremediation works.

Evaluation and analyzing MACH's COD, BOD, acetic acid, iso-butyric and iso-valeric concentrations and pH values in leachate emissions, verified that higher short-term risk of environmental contamination by leachates present cell 1 and 4 than 2, 3 ones. Based on the results of Tables 1-3, it is clear that high and long-term involved risk of environmental contamination by leachate and landfill gas emissions exists in MACH cells, where there is a high fermentable and untreated disposed waste fraction in the waste mass. On the other hand, Cell 1 and 3 present the highest initial short-term risk than the rest ones, but do not present any long term risk in terms of iso-valeric and acetic acid, as greater carbon and organic acid depletion rate exists in them than at the rest ones.

However, except the above evaluation combinations of landfill emissions' behaviour, should be taken into account an additional spatial risk assessment of a probable increased leachates' head flood, following a proper confrontation methodology so as to avoid any particular chemical fluxes on given topographies from the waste mass to the surrounded environment. In the case migration has been made due to a sudden increased leachate head flood then the proper application of numerical analysis for the solution of advection and diffusion phenomena should be made for the proper lining of spatial management works for any migrated landfill emissions. Any available chemical field data should be collected in this case, which are necessary so as to be combined with any other available numerical models, Geographic Information Systems and mapping monitoring data on a given landfill topography so as to take the right reclamation and bioremediation works in time[9,16-18].

However, in order to avoid any migration of leachate toxic chemical discharges to the environment, due to a high leachate flood head, the determination of probable leachate leakage underneath liner's layers should be made after the right application of geomembrane and clay depth on the ground surface, respectively. The necessary spatial associated risk assessment parameters, which should be calculated and to be applied properly on the bottom of a landfill topography or collateral to the particular landfill boundary ground morphologies are the next: the hydraulic conductivity of chemical fluxes in porous media; the annual leachate chemical discharge (L/m^2) and the arrival time of pollutant's concentration front - pollutant transfer, advection and diffusion (years).

Assuming that the leachate chemical flood head is 10 m, after the drainage system collapse due to a big sudden flood event and that the total liner layer is completed by a clay layer 1 m depth and a geomembrane with 1.5 mm thickness, then the vertical hydraulic load inclination will be $i = \frac{\Delta h}{\Delta L} = \frac{h_1 - h_2}{d_{clay}} = \frac{11m}{1m} = 11$; the hydraulic pressure on the upstream surface of the liner layer will be $h_1 = P_{w1}/\gamma_w + z_1 = 10m + 1m = 11m$; the hydraulic pressure on the downstream surface of the liner layer will be $h_2 = P_{w2}/\gamma_w + z_2 = 0m + 0m = 0m$, measuring the z depth from the downstream and assuming atmospheric pressure there

$(P_{w2} = 0)$; taking hydraulic conductivity for the clay material 10^{-9} m/s and for the geomembrane one 10^{-13} m/s, then the vertical hydraulic conductivity for the liner material will be $K_{liner} = \frac{\sum d_i}{\sum \frac{d_i}{K_i}} = \frac{d_{clay} + d_g}{\frac{d_{clay}}{K_{clay}} + \frac{d_g}{K_g}} = \frac{100cm + 0.15cm}{\frac{100cm}{10^{-7}\frac{cm}{s}} + \frac{0.15}{10^{-11}\frac{cm}{s}}} = 6.3*10^{-9}\frac{cm}{s}$; and the respective leachate chemical discharges will be the next for the clay and the liner respectively:

$$Q_{clay} = K_{clay} iA = 10^{-9}\frac{m}{s} * 11m * 1m^2 = 11*10^{-9}\frac{m^3}{s} = 347\frac{lt}{year},$$

$$Q_{liner} = K_{liner} * i * A = 6.3*10^{-11}\frac{m}{s} * 11m * 1m^2 = 6.93*10^{-10}\frac{m^3}{s} = 22\frac{lt}{year},$$

assuming that for the examining hydraulic inclinations is valid that i (geomembrane) ≃ i (clay).

The next risk assessment step should be the determination of the needed time for an investigated leachate migrated concentration, which will pass the liner layer. Below is taken place a relative security investigation risk assessment, assuming a probable chemical leachate C concentration of an examining organic acid migrated concentration (*i.e.* iso-valeric acid, acetic acid *etc.*) equal to C = 0.001 Co, where Co is the initial examining chemical concentration as it was measured before its passing through the liner layer and its migration outside from the landfill boundaries. The latter examining spatial risk assessment problem for the investigating C chemical concentration plume flux is described by the following eqn. 1.

$$\frac{\partial C}{\partial t} = \left(\frac{D}{n}\right)\frac{\partial^2 C}{\partial x^2} - \left(\frac{v}{n}\right)\frac{\partial C}{\partial x} \tag{1}$$

However, the analytical solution of eqn. 1 is given by the following eqn. 2.

$$C(x,t) = \frac{C_O}{2}\left\{ erfc\left(\frac{x - \frac{\bar{v}}{n}t}{2\sqrt{\frac{D}{n}t}}\right) + \exp\left(\frac{\bar{v}}{D}x\right) * erfc\left(\frac{x + \frac{\bar{v}}{n}t}{2\sqrt{\frac{D}{n}t}}\right)\right\} \tag{2}$$

where, for distance x=0, chemical concentration C equals to the initial one Co, C = Co

$$erfz(z) \equiv 1 - erf(z) = 1 - \frac{2}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{(-1)^n z^{2n+1}}{n!(2n+1)}$$

D = diffusion coefficient, is assumed that D = 32 cm^2/year; n porosity of the porous medium, is assumed that n_{clay} = 0.4; $n_{geomembrane}$ = 0.02; $\bar{v}$ = mean velocity of the investigating C chemical concentration; t = time to reach a defined spatial threshold the investigating C chemical concentration (years); for the clay layer there will be $\bar{v} = 2.75*10^{-6}\,cm/s = 86.7cm/yr$, $\frac{\bar{v}x}{D} = \frac{86.7*100}{32} = 271$; for the liner layer there will be $\bar{v} = \frac{6.9*10^{-8}\,cm/s}{0.4} = 5.44cm/yr$, $\frac{\bar{v}x}{D} = \frac{5.44*100}{32} = 17$.

According to the above, taking for C = 0.001 * 415 = 415 µg/L iso-valeric acid concentration and applying the above data there will be for the clay layer only t = 0.76 years (*ca.* 9 months) or for the total liner layer t = 6.7 years, where t is the time to reach the investigating C chemical concentration to the bottom of the examining layer depth, either it is only the clay layer or the total liner layer for both the clay one and geomembrane one. If there will not be installed a proper drainage security system underneath the landfill bottom for the proper collection and treatment of any toxic landfill emissions, then a probable accumulation of several toxic concentrations will take place there and provoking several hazards to public health with associated spatial environmental impacts. In such latter case the proper monitoring ISO environmental quality standards and proper reclamation, bioremediation lined technical works with good timing should take place so as to avoid any environmental impacts, taking into account the above relative calculated clay or liner layers' times so as to take any emergency activities in time when a landfill operational accident has been found[10-12]. Similar spatial investigation calculations could be made and for other chemical concentrations, (*i.e.* COD, BOD, other organic acids' concentrations, heavy metals, *etc.*).

Hence, the lining of a right dense drainage pipe network system underneath the landfill bottom should be installed within a proper set up of monitoring sensors, giving any relative signals of probable leakage of leachates to the main control room of a landfill site. Furthermore, a monitoring network of boreholes should take place in a distance of 20 m next to landfill boundaries for landfill emissions' measurements and security in case of a probable further collapse of the liner layer due to extreme flood events in combination to other simultaneous natural disasters. In case that has been found an extended migration of landfill emissions to the surrounded area next to landfill boundaries' environmental receptors then the lining of a dense monitoring network should be installed properly, following the relative ISO standards, emergency lining methods in order to avoid the migration of any probable toxic chemical hazard to the environment[10-12].

Conclusion

According to the present experimental field data of acetic acid, iso-valeric acid, COD, BOD and of pH, a very good organic depletion presented cell 1 and 3, minimizing

any associated environmental risks in short time period. At Mid Auchencarroch, it was clear that the co-disposal with inert material is sustainable as well as the pre-treatment by wet pulverization since the recirculation of leachate expedite the waste biodegradation.

All the examining chemical concentrations and pH values present great reduction and nearly neutral environment respectively (pH = 7), in the first 12 months, showing that MACH site was stabilized successfully in short time period. Hence, anaerobic batch landfill bioreactors could be used as efficient sustainable landfill sequential batch bioreactor designs. However, an efficient landfill emissions' contamination control could be achieved by a proper installation of a landfill bottom drainage system. A dense lining of landfill emissions' monitoring network and probable bioremediation works next to landfill boundaries based on the above presented risk assessment liner's behaviour evaluations and taking into account particular landfill topographical characteristics and waste input materials. Moreover, a relative flood risk assessment modeling and mapping of needed infrastructure works at a landfill site's topography is recommended for the development of the proper reclamation, confrontation works to any related hazards. Therefore, following properly all the above there will be an efficient minimization of any associated risks and any related environmental impacts next to landfill topographies.

ACKNOWLEDGEMENTS

The authors would like to thank U.K. Energy Technology Support Unit (ETSU), U.K. Department of Trade and Industry (DTI), U.K. Environment Agency (EA) and University of Strathclyde for their support of the Mid Auchencarroch experimental project. The conclusions expressed herein represent the findings of the authors and are based on their expertise and experience in this topic area and their findings in the professional literature. It does not necessarily represent the views of EA, or of the participants in the Mid Auchencarroch Experimental Project.

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(*Received*: 9 June 2008; *Accepted*: 21 January 2009) AJC-7151