



In situ heavy metal attenuation in landfills under methanogenic conditions

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Received 10 September 2002; received in revised form 14 November 2002; accepted 16 November 2002

Abstract

The purpose of this research was to determine the fate and behavior of heavy metals co-disposed with municipal waste under methanogenic conditions. Two landfill simulating reactors, one with leachate recirculation and the other without, were operated in a constant room temperature at 32 °C. These reactors were filled with shredded and compacted municipal solid waste having a typical solid waste composition of Istanbul region. After the onset of the methanogenic conditions, the selected heavy metals including iron, copper, nickel, cadmium and zinc were added according to the amounts suggested for co-disposal under the directives of the Turkish Hazardous Waste Control Regulations. The results of the experiments indicated that about 90% of all heavy metals were precipitated from the reactors within the first 10 days due to the establishment of highly reducing environment and the formation of sulfide from sulfate reduction which provided heavy metal precipitation. No inhibition to the biological stabilization was observed.

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Keywords: Co-disposal; Heavy metal attenuation; Solid waste stabilization; Leachate recirculation; Sulfides

1. Introduction

The generation of both municipal and industrial solid wastes has increased in parallel to rapid industrialization. Effective management of these wastes has become a major social and environmental concern. One of the important waste management strategies is co-disposal, which is a technique for the controlled disposal of industrial wastes together with municipal solid wastes. The result of the comingling of wastes is a decrease in the cost of waste disposal [1]. However, prior to co-disposal, attention must be given to the determination of the types of waste to be accepted, the loading rates and the design of the sites to provide containment for proper management of gaseous and liquid emissions [2,3].

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The major sources of heavy metals in landfills are the co-disposed industrial wastes, incinerator ashes, mine wastes and household hazardous substances such as batteries, paints, dyes, inks, etc. [4]. The most common heavy metals in landfills are iron, cadmium, copper, zinc and nickel [5]. The solubility of metals in leachate depends on the pH, the redox potential, and the solubility of the deposited metal species, concentration of complexing agents ($\text{NH}_3/\text{NH}_4^+$, humic acids) and ion strength [4]. Metal solubilities in the leachate increase as pH decreases. The highest metal concentrations are observed during the acid formation phase of waste stabilization when pH values are low. Therefore, methanogenic conditions and neutral pH must be established within the landfill site to form insoluble metals in the reducing atmosphere before the co-disposal commences [1,2]. Under methanogenic conditions, soluble metals precipitate as insoluble sulfides, carbonates, hydroxides and possibly phosphates in landfills [6]. However, in the presence of sulfides, most of the heavy metals except chromium form extremely insoluble sulfide salts [7].

Sulfides can be formed during the anaerobic decomposition of solid waste either from sulfur-containing amino acids or by reduction of inorganic sulfur compounds [8]. Dissimilatory microbial sulfate reduction is a process in which certain bacteria use sulfate as the electron acceptor in the oxidation of organic matter. *Desulfovibrio* and *Desulfotomaculum* are two genera of sulfate-reducing bacteria [9]. It is known that sulfate reduction and methane production can occur in the same environment. Sulfate reducing bacteria (SRB) have a thermodynamic advantage over the methane producing consortia. Therefore, SRB out-compete the methane-producing consortia for available substrates and sulfide toxicity will be more severe for methane producers [10]. On the other hand, they play an important role in the removal of heavy metals in anaerobic systems.

When organic sulfur compounds are decomposed by bacteria, the initial sulfur product is generally H_2S . Although a fraction of sulfide escapes in anaerobic systems in the biogas, the majority of sulfide remains dissolved in solution as either $\text{H}_2\text{S}_{(\text{aq})}$ or HS^- [11]. $\text{H}_2\text{S}_{(\text{aq})}$ is in equilibrium with $\text{H}_2\text{S}_{(\text{g})}$ and when pH increases, $\text{H}_2\text{S}_{(\text{aq})}$ is converted to HS^- . The dissolution of H_2S in water forms the following equilibrium.



Depending on the pH, the percentage of unionized H_2S drops from 90% at pH 6.0 to 50% at pH 7.0 and to 10% at pH 8.0 [12]. Total dissolved sulfide concentrations ($\text{H}_2\text{S} + \text{HS}^- + \text{S}^{2-}$) of 145–200 mg S/L cause inhibition of sulfate reducing bacteria (SRB) and methane producing bacteria (MPB) in anaerobic systems [13]. Metal-sulfide precipitation as indicated in Eq. (2) is the major factor controlling biological inhibition [14].



where Me is taken as the symbol for a metal.

In this research, metal-sulfide precipitation as one of the major attenuation mechanisms of heavy metals was examined during the methanogenic phase of solid waste decomposition to better understand the attenuation capacity of co-disposal landfills. The effect of various leachate recirculation regimes on the attenuation of heavy metals was also investigated.

2. Materials and methods

2.1. Configuration of the simulated landfill reactors

Two 96-l PVC reactors, one for single pass leaching and the other for leachate recycle, were operated in a constant room temperature at 32 °C. The design and operational features of the landfill reactor with leachate recycle are as shown in Fig. 1.

Each reactor had a diameter of 0.35 m and a height of 1.0 m. The reactors were equipped with three ports; one port was used for leachate drainage and sampling while the other two inlet/outlet ports were used at the top lid to collect gas samples and to add liquid by using a distribution system made of PVC. A 2-l cylinder placed in the vessel in an inverted position and filled with confining solution was used for the measurement of daily gas production.

2.2. Characteristics of the waste matrix

Each reactor was loaded with 13 kg of synthetically prepared, shredded and compacted solid waste mixture and 1 l of anaerobic digested sludge obtained from Tekel Liquor Factory in Beykoz, Istanbul. The synthetic solid waste mixture representing typical solid waste composition of Istanbul consisted of 76% food, 12% paper, 4% plastics, 4% textiles, 3% yard wastes by weight. Preliminary analysis of waste samples and digested sludge indicated

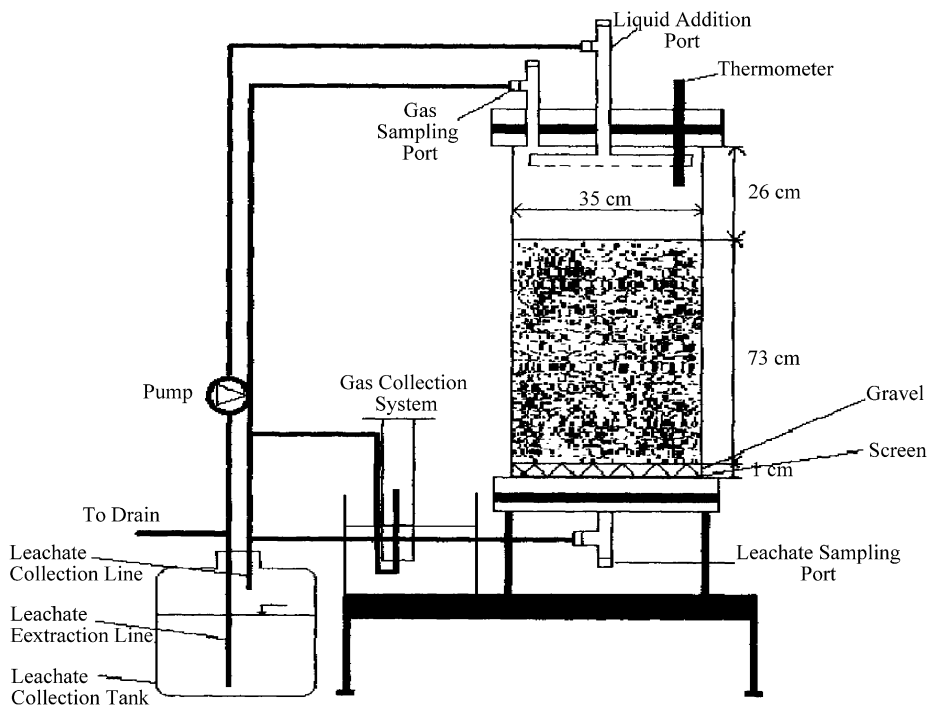


Fig. 1. Design and operational features of the reactor with leachate recycle.

Table 1
Operational stages of the recycle reactor

Stages	Days	Moisture addition (ml)		Addition frequency		Other additions
		Leachate	Water	Leachate/ week	Water/ week	
(I)	0–103	1000	500	1	1	Between Days 56 and 84, 200 ml 1 N KOH
(II)	103–138	1000	500	2	1	Recycle from SP to RR ^a
(III)	138–170	1000	500	3	1	Between Days 142 and 156, 100 g/l Na ₂ CO ₃
(IV)	170–307	1000	500	1	1	On Day 245, 1 l metal solution

^a SP, single pass reactor; RR, recycle reactor.

a solid waste moisture content of 80% and the volatile solid content of the anaerobic sludge was 88% [15].

2.3. Simulated landfill reactors operation

The experimental period was divided into two phases. In the first phase, the onset of methanogenic conditions for both reactors, in which recycle reactor was in the acidogenic phase and single pass reactor was in the initiation of methanogenic phase, was designed to prevent metal solubilization under acidogenic conditions. In the second phase, the selected heavy metals (Fe, Cu, Ni, Cd, Zn) were loaded into the reactors according to the Turkish Hazardous Waste Control Regulations [16]. Tables 1 and 2 show the operational stages of recycle and single pass reactors, respectively.

As indicated in Table 1, the reactor was operated using a weekly recirculation of 1 l leachate and 500 ml water, corresponding to an equivalent of 20 cm per year rainfall (Stage (I)). In the Stages (II) and (III) of our experiments, the recirculation frequency was increased from one to two, and finally three times per week. To accelerate waste stabilization and prevent possible acid inhibition on the methanogens, a buffer solution of 1 N KOH was used to the end of the Stage (I) and 100 g/l Na₂CO₃ solution was added throughout the Stage (III). Moreover, in the Stage (II), an innovative leachate management strategy was employed by using leachate recirculation from the single pass reactor into the recycle reactor to introduce necessary inoculum and nutrients for the acceleration of waste stabilization. In the Stage (IV), the recirculation frequency was readjusted to once a week since desired

Table 2
Operational stages of the single pass reactor

Stages	Days	Water addition (ml)	Frequency/week	Other additions
(I)	0–114	500	1	–
(II)	114–205	500	1	Leachate recycle from RR
(III)	205–245	0	–	No simulated rainfall addition
(IV)	245–307	500	1	On Day 245, 1 l metal solution

Table 3
Masses of the selected heavy metals loadings into the reactors^a

Selected heavy metals and their salts	Metals (g)	Metal salts (g)	Sulfide (g)	Turkish Regulations (g/t MSW) ^b
Cu/CuSO ₄ ·5H ₂ O	1.3	5.1070	0.6560	100
Ni/NiSO ₄ ·6H ₂ O	1.3	5.8205	0.7087	100 ^c
Cd/CdSO ₄ ·2.5H ₂ O	0.13	0.2930	0.0370	10
Fe/(NH ₄) ₄ Fe(SO ₄) ₂ ·6H ₂ O	2.0	14.0040	2.2856	200
Fe/FeCl ₃ ·6H ₂ O	0.6	2.8960	–	–
Zn/ZnCl ₂	1.3	2.7089	–	100

^a g metal/kg wet shredded municipal solid waste.

^b MSW: municipal solid waste.

^c The Regulation does not suggest a special amount for nickel but it suggests 100 g/t for all heavy metals as a general approach.

anaerobic conditions in the recycle reactor were established. The single pass reactor was operated with the addition of 500 ml of water for rainfall simulation. Due to the washout of the required organic carbon sources for methanogens in the single pass reactor, additional leachate was recycled from the recycle reactor to provide necessary substrate (Table 2).

In the second phase, after the onset of the methanogenic conditions reflected high gas production and low COD concentration (Days 245), heavy metal solutions (Fe, Cu, Ni, Cd, Zn) were prepared and introduced into the reactors according in the amounts suggested for co-disposal under the directives of the Turkish Hazardous Waste Control Regulations to prevent the inhibition on microorganisms. Sulfate salts of the selected heavy metals except for zinc were used for the preparation of the heavy metal feed solution in order to introduce the required sulfate into the system. The sulfide toxicity level of 200 mg/l was taken into account to control the inhibition after sulfate reduction to sulfide took place before the loading [17]. Table 3 presents the calculated theoretical masses of heavy metals. The second column of the table indicates the total amounts of heavy metals added to the reactors according to the Turkish Regulation; the third column is the required salt amounts of these heavy metals. The stoichiometric amounts of sulfides to be generated under these sulfate metal salts addition were calculated and given in column 4.

2.4. Sampling and analytical methods

The collected leachate and gas samples were monitored on a regular basis to track the fate of the selected heavy metals and their effects on solid waste stabilization. Leachate samples collected at the bottom of the single pass and recycle reactors were analyzed for chemical oxygen demand (COD), pH, oxidation–reduction potential (ORP), conductivity, alkalinity, sulfate, sulfide, phosphate, chloride and the selected heavy metals (Fe, Cd, Ni, Zn, Cu). All these analyses were performed in accordance with Standard Methods for the Examination of Water and Wastewaters [18]. Metal analyses were performed by using a Perkin-Elmer AAnalyst 300 atomic absorption spectrophotometer. Prior to the analysis, each sample was digested with concentrated HNO₃ and HCl (1:1) according to the ASTM (3010) Standard Method. The gas composition (methane and carbon dioxide) was determined using a gas

chromatograph (GC), Shimadzu-9A equipped with a thermal conductivity detector (TCD) and a 2-m mesh Propac Q column.

3. Results and discussion

Initial leachate concentrations in both reactors prior to the commencement of the experimental study are given in Table 4. As indicated in the table, the initial conditions in the single and recycle reactors were methanogenic and acidogenic, respectively.

Gas volume and leachate chemical oxygen demand were monitored as the main indicators of the progression of solid waste stabilization. The initial gas production rate and leachate COD concentration in the recycle reactor were 500 ml and 10,000 mg/l, respectively (Fig. 2). With the leachate recirculation having a high organic content of about 26,000 mg/l, a sharp increase in leachate COD concentrations was observed. The addition of 1 N KOH buffer solution did not provide any change in waste stabilization. A decrease in COD concentration and increase in the daily gas volume was observed during the Stage (II) along with leachate recirculation from the container of single pass reactor with low organic content and high buffer capacity. During the Stage (III), the addition of Na_2CO_3 with three times

Table 4
Initial leachate characteristics of the reactors

Parameter	pH	ORP (mV)	COD (mg/l)	Alkalinity (mg/l)	Sulfate (mg/l)	Sulfide (mg/l)	Chloride (mg/l)	PO ₄ -P (mg/l)
Single pass reactor	7.78	-174	1159	4038	0	12	371	56
Recycle reactor	5.61	-137	10020	2493	0	40	410	171

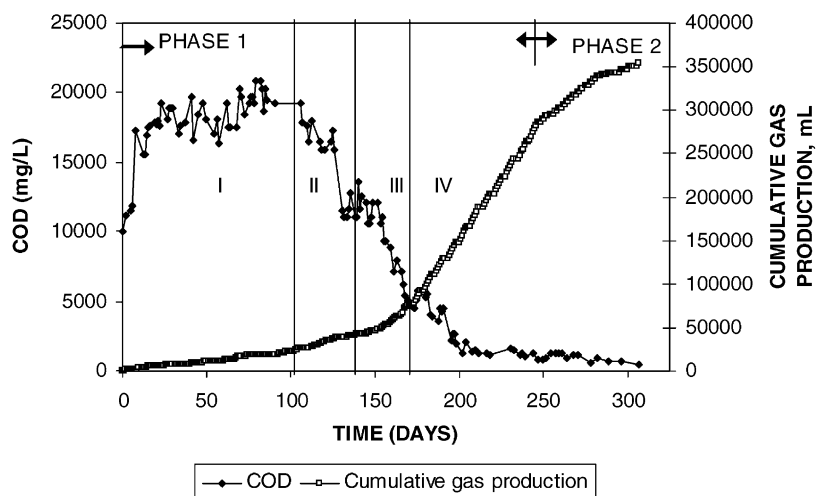


Fig. 2. Leachate COD concentrations and cumulative gas production in the recycle reactor.

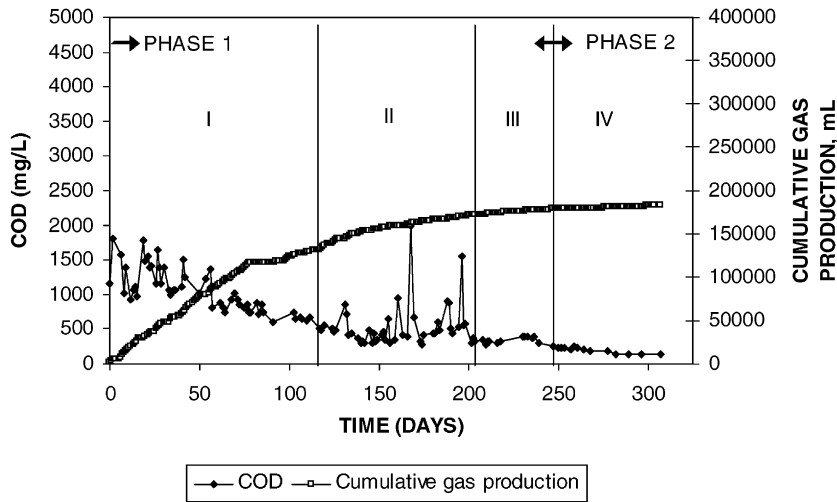


Fig. 3. Leachate COD concentrations and cumulative gas production in the single pass reactor.

per week leachate recirculation accelerated the conversion of organic material to methane and carbon dioxide due to the prevention of the accumulation of volatile organic acids by pH neutralization.

After Day 200, significant decreases in COD concentrations were not observed and the gas production rate reached its highest value of approximately 5000 ml per day. At the end of the study, cumulative gas production rate was 354 l. In contrast to the recycle reactor, organic strength in the single pass reactor was approximately 1000 mg/l (Fig. 3) and a decrease in daily gas production was observed due to nearly completed stabilization of the readily degradable organic carbon sources. The COD concentrations of the single pass reactor decreased to almost 511 mg/l on Day 117. The daily gas production rate and leachate COD concentrations remained approximately constant (100 ml and between 358–290 mg/l, respectively) and the cumulative gas production in the single pass reactor reached 183 l. During Phase 2, after the addition of selected heavy metals, waste stabilization continued in both the reactors without any heavy metal inhibition. As indicated in Figs. 2 and 3, COD concentrations in the recycle and the single pass reactors decreased from 1309 mg/l on Day 245 to 430 mg/l on Day 307 and from 290 mg/l on Day 245 to 138 mg/l on Day 307, respectively. Moreover, the gas production rate and its composition during the operation was constant confirming the continuity of biological activity even in the presence of heavy metals.

In the recycle reactor, the initial methane concentration was approximately 12% (Fig. 4). An increase in the methane concentration after the increase in leachate recirculation frequency from two to three times per week together with buffer addition was observed during the Stage (III). After the onset of methanogenic conditions in the recycle reactor, the methane concentration reached 71% at the end of the experiment. On the other hand, in the single pass reactor, a high initial methane concentration of 73% (Fig. 5) was observed due to the established methanogenic conditions. Methane production decreased to 51% at the end of

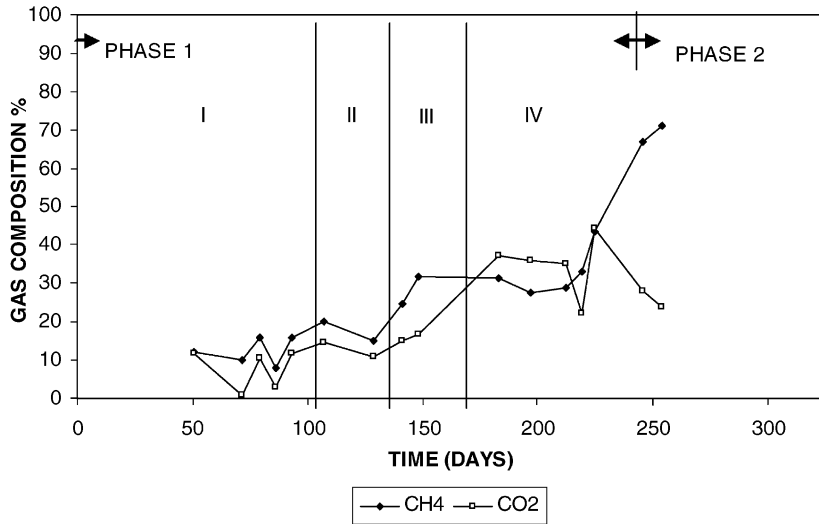


Fig. 4. Gas composition in the recycle reactor.

the study due to the washout of organic carbon from the system. The cumulative volume of methane produced in the recycle reactor and the single pass reactor were 145 and 125 l, respectively.

The changes in leachate pH and alkalinity are as shown in Figs. 6 and 7. During Phase 1, the initial pH and alkalinity values in the recycle reactor were 5.61 and 2493 mg/l as CaCO_3 , respectively. Along with the addition of 1 N KOH, the pH and the alkalinity of the

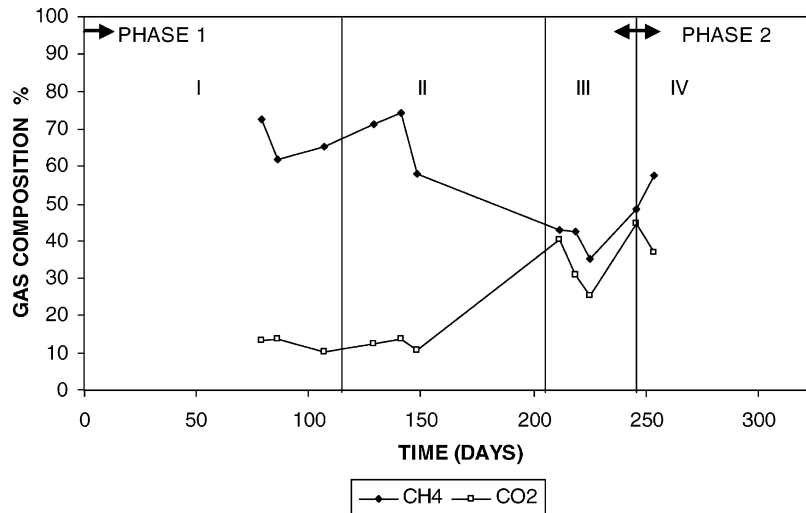


Fig. 5. Gas composition in the single pass reactor.

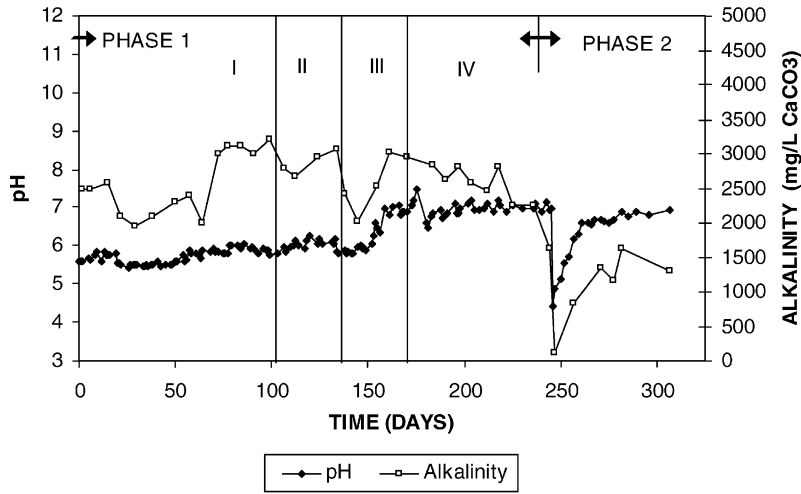


Fig. 6. Leachate pH and alkalinity concentrations in the recycle reactor.

system increased to 6.04 and 3100 mg/l as CaCO₃, respectively, on Day 86. The alkalinity decreased to 2020 mg/l as CaCO₃ on Day 145. With the addition of Na₂CO₃ buffer solution, the pH values rose from 5.80 to 6.98 on Day 159 and alkalinity increased to 2946 mg/l as CaCO₃. After the onset of desired conditions, pH and alkalinity values in leachate remained constant until the end of the study. On the other hand, in the single pass reactor, initial pH and alkalinity values were approximately 7.78 and 4000 mg/l CaCO₃, respectively. Although a slight increase was observed at the end of the Stage (III), the pH of the single pass reactor was constant (6.90) and alkalinity was 2531 mg/l as CaCO₃ at the end of the first phase. Along with metal addition, the pH of the recycle reactor and the single pass reactor decreased

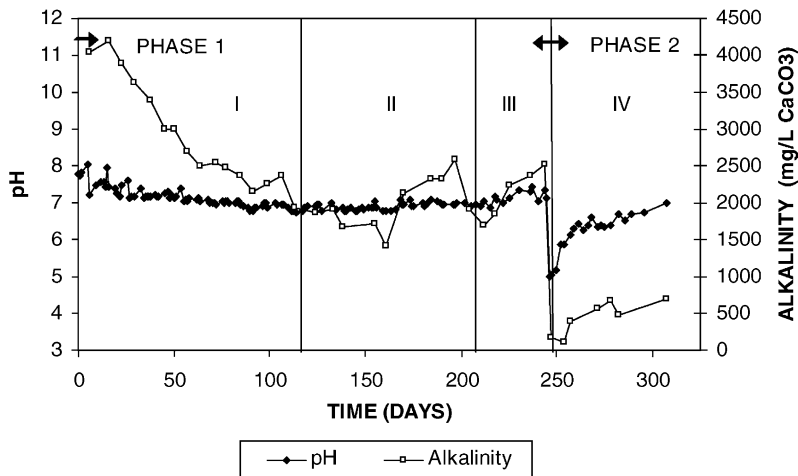


Fig. 7. Leachate pH and alkalinity concentrations in the single pass reactor.

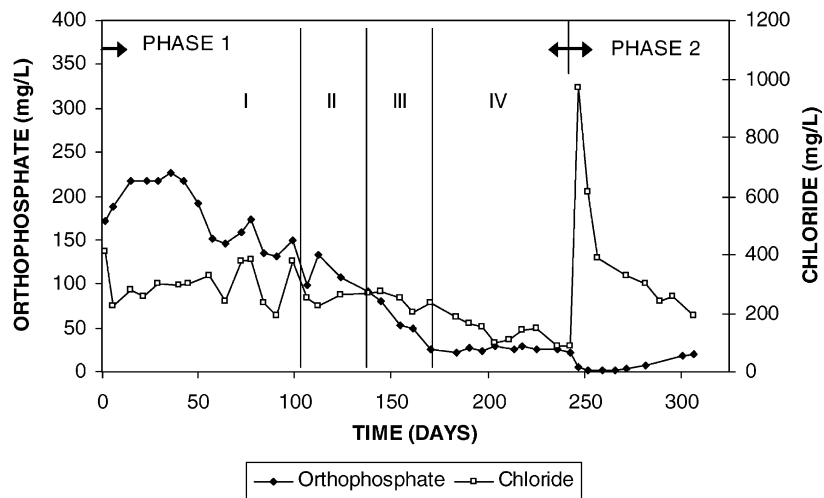


Fig. 8. Leachate PO₄ and chloride concentrations in the recycle reactor.

from neutral to 4.43 and 4.98, respectively. Alkalinity concentrations declined nearly to zero due to the addition of metal solution having acidic properties and precipitation of CO₃²⁻ ions contributing to alkalinity. After the establishment of sulfate–sulfide equilibrium in the reactors, the precipitation of heavy metals was controlled by sulfide and subsequently, the pH of recycle and single pass reactor increased to 6.93 and 6.98, respectively, and alkalinity concentrations of recycle and single pass reactor increased to 1300 and 700 mg/l as CaCO₃, respectively, at the end of experiments.

The initial concentration of orthophosphate in the recycle reactor (Fig. 8) was 171 mg/l. It increased to approximately 226 mg/l due to the leachate recirculation containing high orthophosphate concentrations. However, orthophosphate concentrations began to decrease as a result of orthophosphate assimilation by microorganisms and reached to 25 mg/l during the Stage (IV). On the other hand, the orthophosphate concentrations in the single pass reactor decreased from 56 to 39 mg/l towards the end of Phase 1 (Fig. 9). During Phase 2, the initial concentration of orthophosphate in both the reactors was similar indicating the uniformity in both the reactors. After the addition of the metal salts, a sharp decrease in orthophosphate concentrations was observed in both the reactors as a result of precipitation with heavy metals. However, even these low concentrations of orthophosphate were enough for the maintenance of microorganisms in the reactors. Through the end of the study, an increase in leachate orthophosphate concentrations from the recycle reactor was observed after the reduction of sulfate to sulfide, and the formation of insoluble metal-sulfide precipitates. On the other hand, there was no change in the leachate orthophosphate concentrations from the single pass reactor due to washout of sulfate and insoluble orthophosphates from the system.

Chloride was monitored as a conservative tracer in order to estimate the dilution and evaporation effects (Figs. 8 and 9). The chloride concentration of the recycle reactor stayed approximately constant until the Stage (IV). After Day 170, the chloride concentration decreased slowly due to the dilution effect of water used for rainfall simulation. In contrast

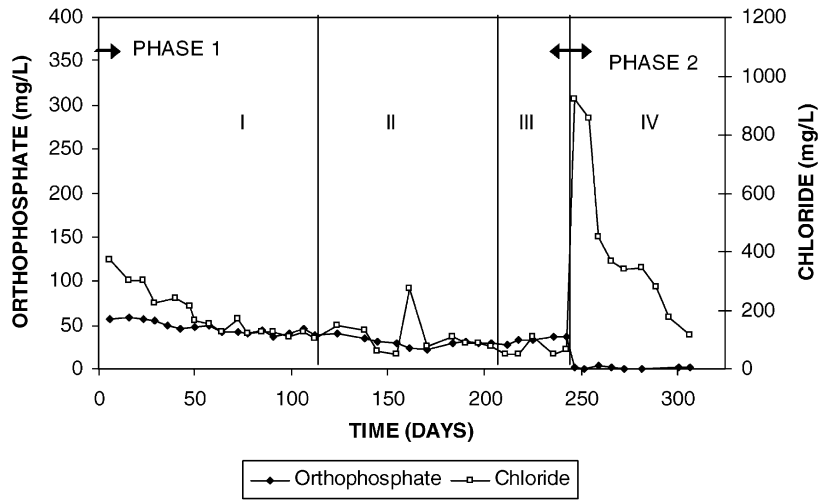


Fig. 9. Leachate PO_4 and chloride concentrations in the single pass reactor.

to the recycle reactor, the chloride concentration in the single pass reactor dramatically decreased due to washout and then stayed constant during Phase 1. Along with the addition of metal solutions into the reactors, chloride concentrations of recycle and single pass reactors increased to 971 and 923 mg/l, respectively, due to the chloride salts of the added metals (such as FeCl_3 , and ZnCl_2). After the sudden increase in chloride concentration in both the reactors, a sharp decrease was observed as a result of washout.

Initial oxidation–reduction potential (ORP) values in the recycle reactor (Fig. 10) were positive due to the presence of oxygen in the reactor. Reducing conditions were established

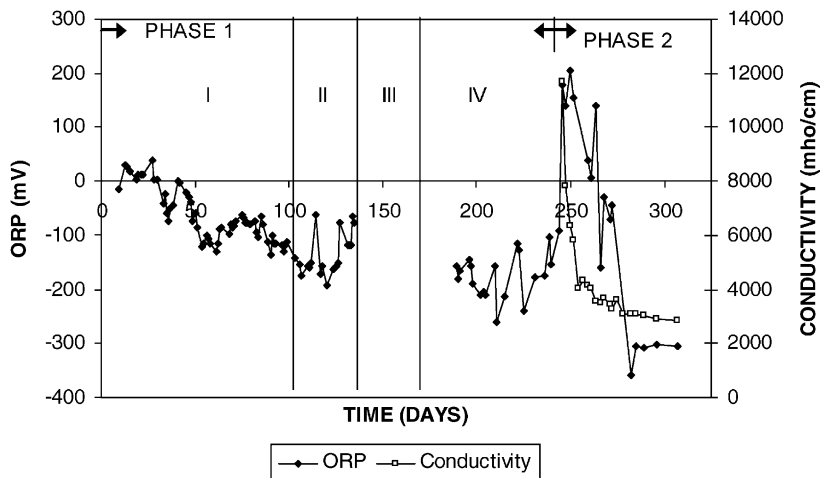


Fig. 10. Leachate ORP and conductivity in the recycle reactor.

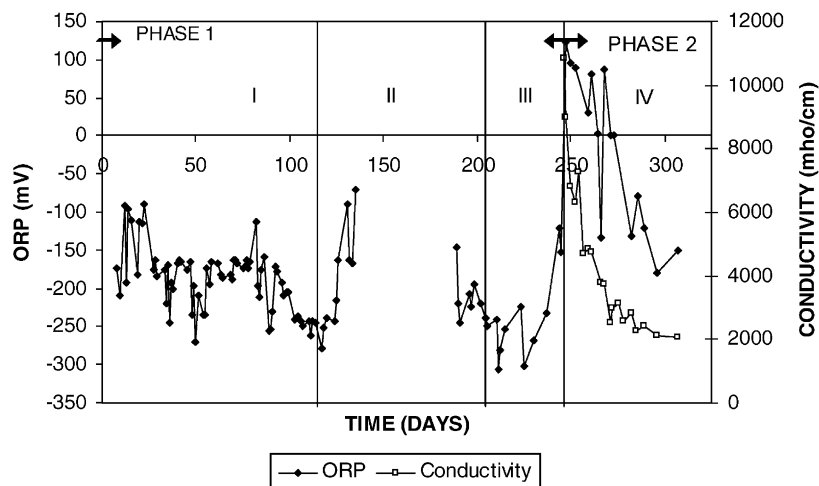


Fig. 11. Leachate ORP and conductivity in the single pass reactor.

by Day 30 and ORP values decreased to -120 mV. Gradual decrease in ORP values continued with an average of about -200 mV until the metal addition. During the same period, ORP values in the single pass reactor (Fig. 11) ranged between -70 and -305 mV. ORP values of single pass reactor were more negative than those in the recycle reactor during Phase 1 because methanogenic conditions in the single pass reactor were established earlier than the recycle reactor. During Phase 2, leachate ORP values became immediately positive and reached $+177$ mV in the recycle reactor and $+123$ mV in the single pass reactor on Day 246, respectively. A transition from the oxidizing environment to the reducing environment was observed on Day 266 in the recycle reactor and on Day 282 in the single pass reactor. The ORP values of the recycle reactor reflected a more anaerobic environment than those of the single pass reactor towards the end of the experiments due to the homogeneity created by leachate recirculation.

The conductivity of a leachate reflects its total concentration of ionic solutes and is a measure of the solution's ability to convey an electric current. In both the reactors, following the addition of metal salts, the change in leachate conductivity with time followed a similar trend; high conductivity values ($11,680 \mu/(\Omega \text{ cm})$ in the recycle reactor and $10,850 \mu/(\Omega \text{ cm})$ in the single pass reactor) decreased to 75–81% of their initial values after 62 days (Figs. 10 and 11). The decrease in conductivity was due to the washout of easily mobilized ions such as metals, chloride and sulfate, combined with factors such as the conversion of sulfate to sulfide under increasingly reducing conditions consequenced by anaerobic biological activity. The subsequent precipitation of sulfide as heavy metal-sulfides would tend to withdraw significant ionic strength from solution.

Sulfate and sulfide concentrations for recycle and single pass reactors are presented in Figs. 12 and 13, respectively. During Phase 1, all sulfur was in the form of sulfide because of the presence of the highly reducing environment in the reactors. Initial high sulfide concentration in the recycle reactor decreased to about 5 mg/l due to precipitation and also

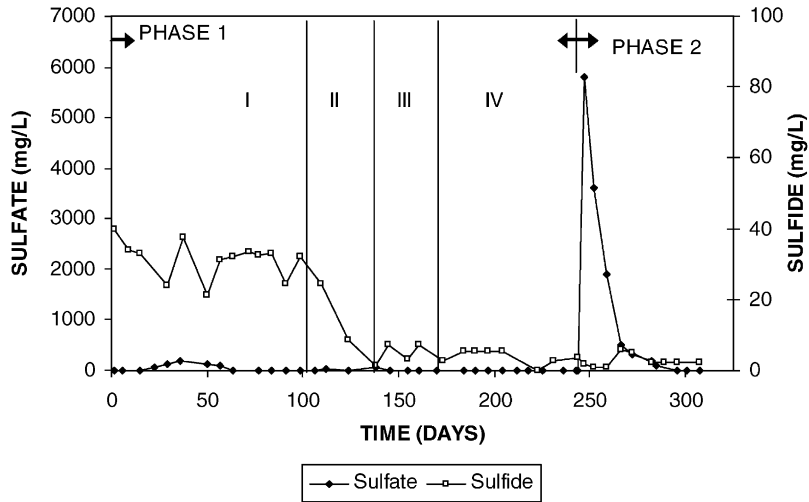


Fig. 12. Leachate sulfate and sulfide concentrations in the recycle reactor.

due to the effect of recirculation from single pass container having low sulfide concentration. After this decline, average sulfide concentration remained constant until the second phase. On the other hand, sulfide concentrations in single pass reactor were lower and removed rapidly from leachate by precipitation and washout mechanisms in the Stage (I). During Phase 2, sulfate concentration increased immediately in both the reactors due to the addition of metal-sulfates except for zinc. The sulfate concentrations of the recycle reactor and the single pass reactor were 5800 and 6200 mg/l on Day 247, respectively. As indicated in Figs. 12 and 13, sulfates were reduced rapidly to sulfides. While sulfate concentrations in

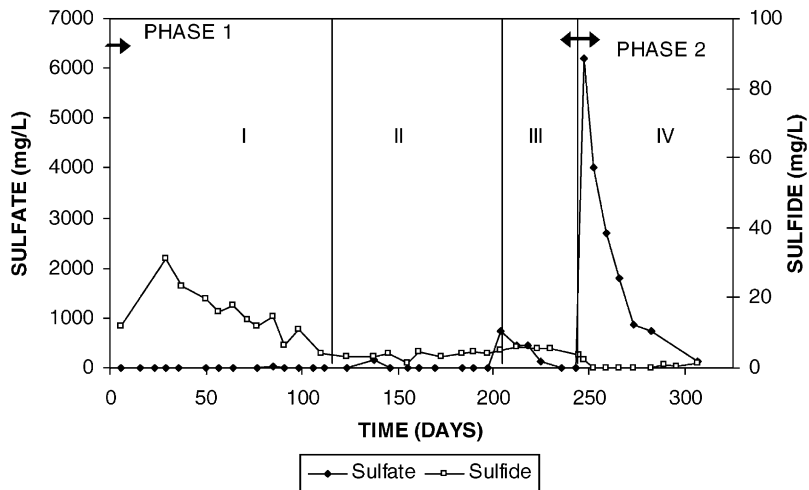


Fig. 13. Leachate sulfate and sulfide concentrations in the single pass reactor.

recycle reactor reached zero on Day 296 due to positive effect of leachate recirculation, sulfate concentration in the single pass reactor was 125 mg/l at the end of experiments. On the other hand, sulfides formed from sulfate reduction were precipitated with heavy metals and after precipitation, the remaining sulfide concentrations were 2.4 and 1.6 mg/l on Day 307 in recycle and single pass reactors, respectively.

The behavior and fate of the selected heavy metals (Fe, Cu, Cd, Ni, Zn) in terms of their mobility in both the reactors under methanogenic conditions received attention in this study. Before co-disposal, the selected metals were monitored several times and insignificant background metal concentrations in both the reactors were found. The selected metals (Fe, Cu, Cd, Ni, Zn) were loaded into the reactors in accordance with the stoichiometric calculations given in Table 3.

Iron was introduced into the reactors in the forms of Fe^{3+} and Fe^{2+} . However, Fe^{3+} ions were reduced to Fe^{2+} in the reactors due to the prevalence of the reducing conditions. Initial leachate iron concentrations in recycle and single pass reactors were 905 and 1436 mg/l, respectively. Approximately 45% of iron in the recycle reactor and 52% of iron in the single pass reactor were precipitated in the first day of operation. The initial precipitation of cadmium, nickel and zinc were lower than the other metals. The precipitation efficiency ranged between 33 and 47% for these metals. The precipitation efficiency of copper in the reactors was much higher than the other metals. The initial precipitation efficiency of copper in recycle and single pass reactors were 56 and 62%, respectively. Sulfide was known to be a very potent precipitant for copper and forms less soluble copper sulfides ($pK_{so} = 44.1$) [19].

The selected heavy metals were monitored for a period of 62 days. As indicated in Fig. 14, approximately 90% of all heavy metals were precipitated from the reactors within the first 10 days due to the establishment of highly reducing environment and the formation of sulfide from sulfate which provides heavy metal precipitation. The measurements of leachate ORP, sulfate, sulfide and conductivity also confirmed the attenuation of the heavy metals during this period. Moreover, the results of the experiments indicated that initially, the solubility of metal was controlled by anions such as sulfate, carbonate and phosphate. Fe^{3+} especially

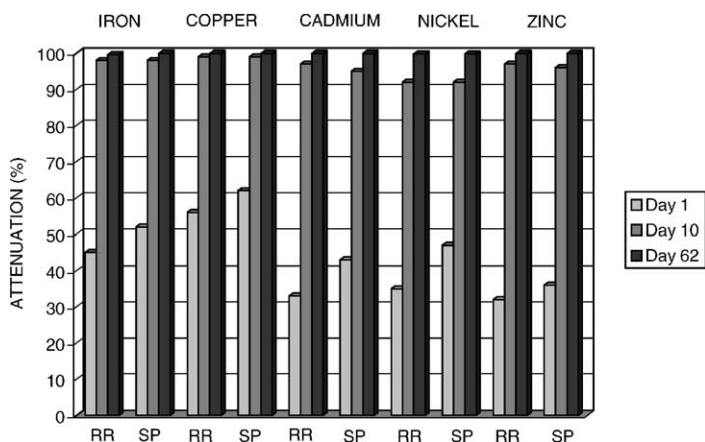


Fig. 14. Removal efficiency of the metals for recycle and single pass reactors.

formed insoluble iron-phosphates together with initial low pH values since theoretically, the minimum solubility of FePO_4 occurs at pH 5.3 [20]. After the establishment of the reducing environment as confirmed by low ORP values, Fe^{3+} and sulfate ions were reduced to Fe^{2+} and sulfide, respectively. Along with the presence of sulfide, all metals formed insoluble metal-sulfides and other ions including carbonate and phosphate became mobilized. These were confirmed by measurements of alkalinity, orthophosphate and sulfide. Leachate recirculation accelerated sulfate reduction and heavy metals formed insoluble metal-sulfide precipitates earlier in the recycle reactor compared to the single pass.

3.1. Mass balance analysis

At the end of the study, mass balance computations were performed to better understand the precipitation of heavy metals by sulfides. The total mass of loaded and effluent metals were calculated. It is rather difficult to make an accurate material balance on heavy metals together with sulfides in landfills due to the presence of many chemical complexes. Metal-sulfide precipitation in both the reactors was determined using the following approach; it was assumed that all sulfate concentrations coming from metal salts reduced to sulfides and the sulfides formed insoluble metal-sulfides.

Mass balances of heavy metals and sulfides calculated stoichiometrically for the first and last days of the study and for Day 10 indicated that the attenuation by sulfide precipitation was approximately 90% for all heavy metals in reactors. The first bars in Fig. 15, indicate theoretical sulfide requirements for metal precipitation calculated from the attenuated metal concentrations in the system for these days. The second bars are stoichiometric amounts of sulfide generated after the reduction of sulfate calculated from attenuated sulfate concentrations in the reactors. As evidenced in Fig. 15, the generated sulfide amounts to precipitate heavy metals was not enough in the first 10 days. Therefore, other anions made contributions to the heavy metal precipitation. On Day 10, while the required sulfide amounts for metal precipitation in the recycle and single pass reactors were 3117 and 3060 mg, respectively,

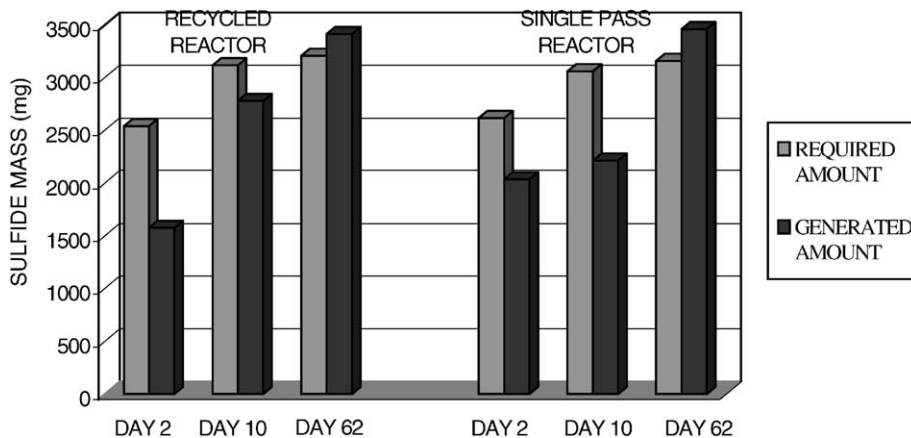


Fig. 15. Stoichiometric sulfide amounts.

the generated sulfide amounts due to sulfate reduction in the recycle and single pass reactors were 2780 and 2214 mg, respectively. After the reduction of all sulfate to sulfide and precipitation of the metals by sulfide compounds, theoretically calculated sulfide amount in the systems was found higher than the measured values at the end of the study. The possible explanation of this discrepancy between measured and calculated sulfide/sulfate masses are the H₂S gases escaping from the system and assimilation of sulfate/sulfide into cell mass, both of which could not be quantified.

4. Conclusions

Based upon experimental results obtained during the experimental study, the following conclusions are provided:

1. Leachate recirculation management strategy offers opportunities for more rapid waste stabilization, including attenuation of co-disposed heavy metals.
2. Utilization of buffer solutions of KOH and Na₂CO₃ together with leachate recirculation further enhanced waste stabilization and prevented possible acid inhibition.
3. The exchange of leachate between reactors provided desirable microbial population, organic carbon and nutrients and enhanced the accelerated waste stabilization.
4. Methanogenic populations within the reactors were not inhibited by the presence of heavy metals at limiting concentrations prescribed by the Turkish Hazardous Waste Regulation.
5. About 90% of all heavy metals were attenuated from the reactors within the first 10 days due to the establishment of highly reducing environment and the formation of sulfides from sulfate reduction which provided heavy metal precipitation.

Acknowledgements

The authors acknowledge the financial support provided by Boğaziçi University Research Fund for the realization of this research project no: BU-99 Y03.

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