DETERMINATION OF THE REMAINING STABILIZATION POTENTIAL OF LANDFILLED SOLID WASTE BY SLUDGE ADDITION

by

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ABSTRACT

Research activities on the innovative landfill management techniques are becoming attractive research areas in the last decades due to increasing amounts of solid waste by increasing industrialization and urbanization.

In these landfill management techniques, determination of the stabilization potential of solid waste and the degree of stabilization at the site play important role because the degree and rate of stabilization in a landfill can be a valuable parameter for future predictions of leachate and gas generation, determination of the feasibility of a landfill methane recovery program, evaluation of the closure time and the final use of the site.

In this study, the remaining stabilization potential of solid waste retrieved from an operating landfill was investigated by the anaerobic digestion of the waste with anaerobically digested sludge with differing sludge:waste ratios. Four reactors were placed in a temperature controlled aquarium and loaded with different sludge:waste ratios in order to determine the remaining stabilization potential, to find the optimum ratio for the highest methane yield and to investigate the use of sludge as an enhancement technique for the waste degradation.

The results of the study suggested that the addition of anaerobically digested sludge was an effective technique for the enhancement of solid waste degradation. Among the different sludge:waste ratios, the highest ratio 1:4 was found the optimum one for the enhancement and for the methane production in the study. The remaining stabilization potential of the retrieved solid waste was determined as 7% at the end of the study.

ÖZET

Katı atık depolama sahaları işletim teknikleri üzerine yapılan araştırma çalışmaları, son yıllarda endüstrileşme ve şehirleşmeyle artan çöp miktarıyla önem kazanmıştır.

Bu işletim tekniklerinde, katı atığın ayrışma potansiyelinin ve sahadaki ayrışma derecesinin tayini önemli rol oynar, çünkü bu bilgiler gelecekteki sızıntı suyu ve gaz miktarının tahmini, depo gazı geri kazanımı projelerinin fizibilitesi, sahanın kapanma süresinin ve sahanın son kullanımının belirlenmesinde önemli parametrelerdir.

Bu çalışmada, sahadan alınmış katı atığın ayrışma potansiyeli farklı oranlarda yapılan anaerobik çamur ilavesiyle araştırılmıştır. Dört reaktör, sıcaklık kontrollü bir akvaryuma yerleştirilmiş ve ayrışma potansiyelinin tayini, en yüksek metan eldesi için uygun olan çamur:katı atık oranının belirlenmesi ve çamur ilavesinin ayrışmayı hızlandırıcı bir teknik olarak kullanımının araştırılması amaçlarıyla dört ayrı çamur:katı atık oranıyla yüklenmiştir.

Çalışmanın sonuçları, çamur ilavesinin katı atık ayrışmasını hızlandırmada etkili bir teknik olduğunu göstermiştir. Uygulanan dört ayrı oran arasında, en yüksek oran olan 1:4 oranının ayrışmanın hızlandırılması ve metan elde edilmesi için optimum oran olduğu belirlenmiştir. Sahanın ayrışma potansiyeli % 7 olarak belirlenmiştir.

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1. INTRODUCTION

Solid waste generation is increasing all over the world with increasing industrialization and urbanization. However, a similar increase can not be observed in the number of waste disposal sites due to difficulties of finding landfill space, public pressure against new landfill sites and tighter landfill regulations. When the problems evolving from old dump sites are added to these, it is evident that the research activities on innovative landfill management and leachate and gas control techniques are becoming attractive research areas.

Determination of the stabilization potential of solid waste and distribution of the already completed stabilization at the site are playing important roles for the development of such innovative management and control techniques. However, the mechanism and degree of this stabilization is uncertain and very difficult to determine.

This uncertainty comes from the criteria of the stabilization; a landfill is considered to be stabilized when maximum settlement has occurred with negligible gas and leachate production without a pollution hazard for the environment. If the dimensions and operation duration of a landfill are taken into consideration; these can not be easily monitored. Therefore, the determination of the remaining stabilization capacity of landfilled solid waste is an important issue in solid waste management.

In this study, the further stabilization of landfilled solid waste is studied by the addition of anaerobically digested sludge to the solid waste with different sludge:waste ratios. This approach enables also to find the conditions for optimum methane formation and to study on the effects of sludge addition on solid waste degradation. In other words, the study may address to an alternative sludge disposal option which could accelerate stabilization and help methane recovery without causing nuisance.

The need for such a research can be explained in a few headings. First of all, uncertainty in the rate and degree of stabilization in the solid waste prevents making credible prediction of leachate and gas generation and developing effective control of these potential sources of pollution. Prediction of leachate and gas generation rates is also useful for the design and operation of bioreactor landfill systems.

Moreover, the potential of the site to generate energy from waste in terms of methane recovery may be predicted with such a study. If landfill gas utilization facility is already utilized at the site, the efficiency of the system may be estimated with the results of the optimization study.

A major problem in determining the stabilization of the solid waste is that the gas has to be monitored over the total decomposition period. Therefore, the solid waste degradation is enhanced in these studies. This is achieved by the utilization of one/some of the enhancement techniques such as leachate utilization, buffer addition, sludge addition etc. Therefore, this approach enables to observe the effects of different enhancement techniques on waste degradation.

The determination of the remaining stabilization potential is also a useful technique to determine the efficiency of leachate management system employed for a landfill site. By evaluating the results of such a study the performance of an existing leachate recirculation program and/or sludge addition could be determined.

In this study, addition of anaerobic digested sludge is used for the enhancement of the anaerobic degradation. By this approach, an alternative disposal of sludge is also investigated. This investigation is also important due to the increased amounts of sludge requiring disposal with the higher water quality standards and improved treatment processes.

The control and enhancement of the waste degradation is very advantageous, because shorter stabilization times will be achieved by this way and gas and leachate generation will be concentrated over a shorter time. As a consequence, higher gas recovery rates, safer conditions and easier reclamation activities will be the asset of this management strategy.

Apart from control and management, the ultimate use of site may also be determined by the findings of these studies. The completed portion of stabilization is determined and the suitable time for closure could also be determined by this technique. The potential ultimate use of the site and post-closure precautions may be decided according to the results.

An application area of the study in the ultimate use of the site may be in the area of landfill mining. Landfill mining is an innovative landfill management system. It is especially promising for countries like Turkey where open dumps are still the common places for ultimate disposal. In landfill mining processes, the disposed solid waste is excavated and items like soil, recyclable materials, landfill space are recovered, the design of the site upgraded in other words liners are repaired or installed if not present. The retrieved solid waste may also be processed by incineration, leachate recirculation etc. At the end, the residues are hauled away or re-landfilled in the prepared site. This approach may be a solution for the need of future landfill sites. The information on the stabilization potential of solid waste retrieved from different locations and depths is required for this application. If the stabilization is found to be completed, the excavation and recovery processes are performed. But if it is not completed yet, the stabilization may be enhanced at smaller controlled units.

All these application areas show the necessity and importance of studies on the determination of the remaining stabilization potential of landfilled solid waste with sludge addition. Therefore, the effects of such sludge addition on solid waste degradation and stabilization of the solid waste were investigated in this study. Analysis of the results of the study provides basis for pilot scale applications and further research.

2. LITERATURE REVIEW

Effective management of solid waste has become an important issue in the last century due to increasing amounts of solid waste by the population increase, environmental problems faced because of unproper waste disposal and increasing public awareness.

This problem is approached within the "Integrated Solid Waste Management" system in many developed countries. The main aim of this system is to minimize solid waste generation and the waste to be disposed after this reduction. The components of an integrated waste management system are source reduction, recycling, waste transformation and landfilling with decreasing rank. Although landfilling is at the lowest rank of this system, it is the most popular and important one among all components since it is the most economically sound and practical one (1).

Sanitary landfill can be defined as an engineered method of disposing solid wastes in a way that doesn't cause nuisance for public health and environment. Even if one of the other alternatives of disposal is in practice, there will still be residual materials for ultimate disposal in landfills. Therefore, apart from the need for waste minimization and recycling, landfills still have to be operated in the future because landfilling is the final step of solid waste management and a necessary element of all waste management systems.

However, it is also known that landfill areas are potential sources of serious environmental pollution because of gas and leachate emissions resulting from the decomposition of solid waste in landfills. Because of these potential sources of pollution, the management of both elements and stabilization in landfills require a deep concern and extensive understanding.

In the literature review section, landfill stabilization, leachate and gas formations, enhancement of landfill stabilization, codisposal of solid waste and sludge will be described.

2.1. Landfill Stabilization Processes

The stabilization processes in the landfill are the key factors for the understanding and controlling of the environmental impacts of the sanitary landfills. Physical, chemical and biological changes in solid waste begin as soon as the waste is disposed to the site and result in the release of landfill gas and leachate. These changes are stated as follows (1); biological decay of putricible material, either aerobically or anaerobically, chemical oxidation of waste constituents, dissolution and transport of organic and inorganic constituents, diffusion and transport of gases, hydraulic liquid transport, settlement etc. The kind and degree of these processes is influenced by the waste composition, available moisture, temperature, inhibiting materials and the rate of compaction (1).

Waste degradation and stabilization within a landfill begin under aerobic conditions and proceed anaerobically. The oxygen is not available in landfills except the surface area and the time of disposal. Therefore, anaerobic conditions dominate in the landfill and control the leachate and gas quality. Most landfills are observed to generate CO_2 and CH_4, indicating that anaerobic conditions are maintained in the waste matrix.

2.1.1 Decomposition of Solid Waste; Microbiology and Biochemistry

Waste degradation in landfills is a process that requires coordinated activity of several groups of bacteria. The establishment and maintenance of a balance among all microorganisms is crucial for the efficient waste stabilization.

Both aerobic and anaerobic processes take place in landfills. If aerobic processes take place, the organic material is mostly converted mainly to carbon dioxide, water and energy (4).

After a short duration of aerobic conditions, anaerobic conditions are observed in landfills. The anaerobic decomposition of solid waste is considered to be a two-stage process; acid formation and methane formation stage. Two stages of anaerobic decomposition are illustrated in Figure 1.

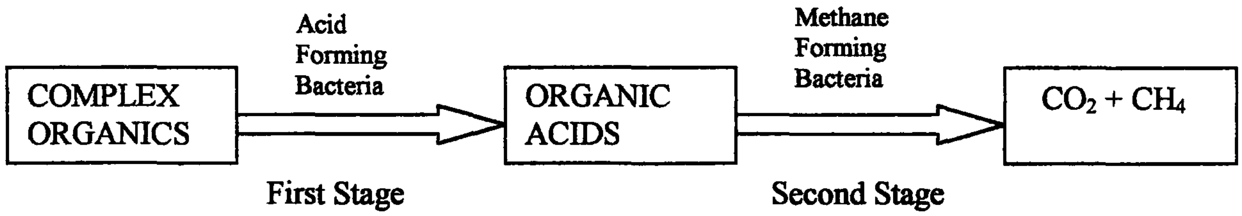

Figure 2.1 Two Stages of Anaerobic Decomposition of Complex Organic Waste

In the acid formation stage, the complex organics are altered by a group of bacteria termed as "acid formers". The first step of degradation is named as acid formation. In this stage, complex materials such as cellulose, fats, proteins and carbonhydrates are hydrolyzed, fermented and biologically converted to simple organic materials mainly organic fatty acids. Alcoholes, methane and carbon dioxide are also produced during this step. The first stage of degradation is required to convert the organic material suitable for the second stage (2). The microorganisms that are active at this stage, "acid formers", are much more tolerant than those of the methane formation stage (6).

At the second stage, "methane formers" convert organic acids into methane and carbon dioxide. The methanogens are obligate anaerobe and operate at very low oxidation-reduction potentials (ORP). They can only utilize a limited number of substrates including acetate, formate, methanol, methyamines and hydrogen plus carbon dioxide (5). There are mainly three pathways for methane generation; methane and carbon dioxide production from acetic acid by aceticlastic bacteria, reduction of carbon dioxide through the addition of hydrogen to form methane and carbon dioxide by carbon dioxide reducing methanogens and finally utilization of formic acid and methanol to produce methane (7). During methane formation of the refuse material, over 70% of the methane originates from acetate (2). The methane formation stage is the stage in which the majority of waste stabilization takes place in landfills.

2.1.2. Phases of Stabilization in Landfills

Five sequential stabilization phases are observed in landfills throughout the life of the site. These phases are Initial Adjustment, Transition, Acid Formation, Methane Formation and Final Maturation Phases (1).

Five stabilization phases of landfills that are indicated with the selected parameters are described below;

Initial Adjustment Phase is the first phase of stabilization and begins with the placement of waste into the landfill. It is the moisture accumulation phase and leachate production is not seen until field capacity is reached. Initial settlement of the waste material is observed with the closure of every cell. The beginning of stabilization processes are detected with the changes in environmental parameters. The solid waste degradation proceeds aerobically at this phase due to the presence of oxygen. The aerobic phase in newly placed refuse lasts for only a few days.

Transition Phase follows the initial phase. Leachate generation is observed in this phase when the field capacity is exceeded. As the disposed waste is covered by other waste material, oxygen depletion occurs very quickly, a transition from aerobic to anaerobic conditions and a trend towards to a reducing environment is observed. The primary electron acceptor shifts from oxygen to nitrates and sulfates with the depletion of oxygen and production of carbon dioxide. Volatile acids appear and an increase in the concentration in leachate is observed.

Acid Formation Phase is the third phase in which the pH begins to decrease due to the accumulation of high quantities of volatile acids in the system. Volatile acid concentrations increase by the continuing hydrolysis and fermentation of waste and leachate constituents. When the pH decreases, an increase in heavy metal concentrations is observed in leachate with mobilization and solubilization mechanisms. Nutrients (nitrogen and phosphorus) are released from the waste and utilized for the support of biomass growth.

In the Methane Formation Phase that is the fourth of the stabilization phases, methanogens convert volatile organic acids (VOA) formed in the acid formation phase to methane and carbon dioxide. The pH of the system increases to neutral with the conversion of VOAs. A highly reducing environment is detected in this phase, the oxidation-reduction potentials (ORP) are at their lowest levels with the accumulation of reducing sulfur and nitrogen species. As the anaerobic conditions are established, excess SO_4^- (sulfate) is reduced to S^- (sulfides) (3). Heavy metals levels drop in leachate by precipitation and complexation with sulfides, hydroxide and carbonate anions (3). The generated sulfides precipitate iron, manganese and heavy metals that were dissolved in the acid formation phase. Nutrient consumption and conversion continues in this phase. Finally, leachate organic strength is decreased in this phase and gas production increases with this decrease.

Final Maturation Phase is the last step of solid waste stabilization. Active microbial activity diminishes at this phase. After the active waste transformation at the fourth phase, biological degradation of readily available organics is completed in the beginning of this phase and the remaining organic material is not easily degradable. Gas production decreases in this step. Microbially resistant organic materials may be slowly converted to humic like substances, these substances form complexes with heavy metals and heavy metal concentrations again drop at this phase. Oxygen and oxidized species may slowly reappear with the increasing oxidation-reduction potential (ORP) values.

The presence, duration and intensity of these phases are identified by the changes of certain parameters in leachate and gas composition. pH and Oxidation Reduction Potential (ORP) are physical-chemical parameters that are monitored for the indication of acid-base condition and oxidation reduction respectively (1). Chemical Oxygen Demand (COD) is a chemical parameter that indicates the organic strength of leachate in terms of the oxygen required for the oxidation of the chemically oxidizable part of the waste (1). The concentration of Volatile Organic Acids (VOA) is another parameter indicative of organic strength of leachate, since the majority of COD is composed of VOA during the Acid Formation Phase. For the monitoring of major nutrients (nitrogen and phosphorous), leachate is analyzed for ammonia nitrogen and orthophosphate respectively. When the gas phase is considered, the gas generated is analyzed for gas composition and for the daily gas production. Chlorine is also analyzed for observing the effect of dilution on waste stabilization.

These phases indicated with selected parameters are illustrated in the Figure 2.2;

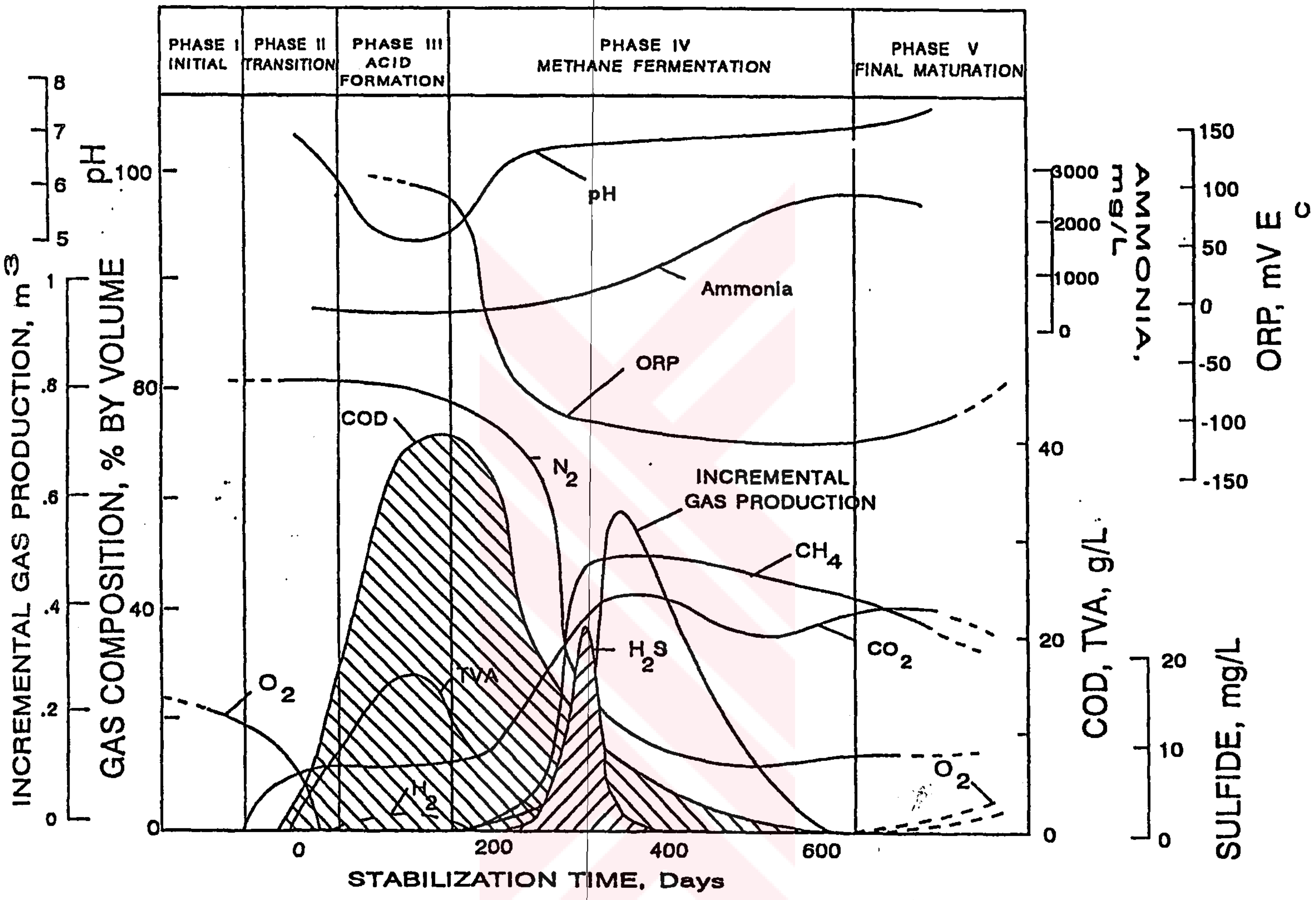

Figure 2.2. Changes in Selected Indicator Parameters During the Phases of Landfill Stabilization (Ref. 29)

2.1.3 Factors Affecting Landfill Stabilization

The main factors influencing the stabilization in landfills are described below;

2.1.3.1 Moisture Content

Moisture content is an important factor in solid waste stabilization. It is added to the landfill by infiltration of rainfall, surface water, bacterial action or in the form of sludge and waste (9).

Moisture is required for the activity of most microorganisms (6). If sufficient moisture is not available in the solid waste, the waste can remain without any decomposition for a long period of time (9). In addition to this, researchers like Chian et. al. concluded that increasing moisture content increased the rate of gas production (11). It is because of the fact that most of the reactions occur in the liquid phase. Moisture content also limits the oxygen transfer from atmosphere and it helps the transport of substrate, nutrients, buffer and dilution of inhibitors and spreading of microorganisms within the waste (13).

High moisture content, in the range of 60 to 80 percent favors maximum methane production (2). But the moisture content of fresh refuse ranges from 15 to 40 percent with a typical value of 20 percent on wet basis (2, 5). Therefore lack of moisture may significantly limit gas production rate in a sanitary landfill.

Distribution of moisture is also an important factor in waste stabilization. Stabilization efficiency is much higher in systems with good moisture distribution with the effect of longer contact time between microorganism and substrate as well as greater amounts of accessible substrate (3).

2.1.3.2 pH and Alkalinity

The microbial stabilization processes in a landfill are also closely affected by the pH and the alkalinity of the system. The pH influences especially chemical processes such as precipitation, sorption, dissolution and redox reactions (12).

During the Acid Formation Phase, an accumulation of organic acids is observed accompanied by a reduction in pH; meanwhile the bicarbonate buffer system is displaced by the volatile acid buffer system (1). This reduction in pH will result in changes in hydrolysis, liquefaction, gas production and encourage mobilization of heavy metals in the system (3).

Although methane formation will proceed in a pH range of 6.5 to 8.0, the optimum pH for methane generation is between 7.0 to 7.2 (2). The pH range for the acidogenic bacteria is much wider than for the methanogenic bacteria due to the delicate nature of methanogenic bacteria. The maintenance of this acceptable pH range mainly depends on the presence of buffering materials where buffer capacity is measured in terms of alkalinity (1). An alkalinity in excess of 2000 mg/l as calcium carbonate is considered as optimum (6). The presence of alkalinity will buffer the system, minimizing sudden changes in the pH and stabilizing the gas production process (2).

2.1.3.3 Temperature

Temperature flux within a landfill plays an important role in regulating landfill stabilization rates and affects the type of bacteria that may be dominant in the landfill. It may also affect the reaction mechanisms and biodegradation rates.

The effect of temperature on methane formation has been studied in the thermophilic, mesophilic and psychorophilic range (6). It is reported that methane production during sewage sludge digestion was possible at temperatures from 0 °C to 50 °C, but maximum production rates occured at specific temperatures within each of the three ranges, 37 °C being the optimal for the mesophilic range (6).

Christensen and Kjeldsen reported that the methane production rate has been observed to increase significantly when the temperature is raised from 20 °C to 30 °C and 40 °C in laboratory simulations of landfill processes (13). Optimum temperature for methane production has been found within the range of 30 to 37 °C (9). It is also found that gas production rates are reduced with deviations from these optimal temperatures (6).

Methanogenesis is exothermic, it is advantageous to increase the temperature in the landfill (6). The heat of methanogenesis is 13 J/kmol and this heat fill warm the fill material and be lost by water evaporation.

It is a fact that temperature within a landfill fluctuates with the influence of ambient temperature and the insulating effects of surrounding solid waste mass (3).

2.1.3.4 Nutrients

The availability of essential nutrients is required for efficient anaerobic waste degradation. The anaerobic decomposition is dependent upon bacteria that require macronutrients, nitrogen and phosphorus in large amounts and micronutrients such as iron, nickel, cobalt, sulfur, calcium, molybdenum, tungsten, selenium and some organics in trace amounts (3,9).

Gas production rates depend on the organic material available for decomposition and optimal ratios between COD, nitrogen and phosphorous are given as 100:0.44:0.08 by Christensen and Kjeldsen (13). In general, municipal landfill is not limited by nitrogen and phosphorous but there may be nutrient-limited spots due to the waste heterogeneity (13). Limiting nutrient in the landfill environment is usually phosphorous as reported by Christensen and Kjeldsen (13).

2.1.3.5 Inhibitors

Inhibition of stabilization in landfills may appear where significant amounts of industrial wastes are codisposed in the site. The studies of anaerobic waste digestion indicate that the methane-forming ecosystem is very sensitive to inhibitory materials. Although the methanogenic group seems the most susceptible to the inhibition, acidogenic group may also be inhibited (13).

Substances that have been found to be inhibitory to the anaerobic degradation include high concentrations of heavy metals, volatile organic acids, sulfide, ammonia and other toxic substances.

Ammonia which is a source of nitrogen for anaerobic bacteria assimilation may be inhibitory at high concentrations. The inhibitory effects of ammonia are caused by free ammonia which constitutes the majority of ammonia nitrogen at pH values higher than 7,2. The inhibitory effects of ammonia are observed at concentrations of 1500 mg/l but the concentrations above 3000 mg/l causes termination in gas production.

Although trace amounts of heavy metals are necessary for microbial population, they may be inhibitory to the system above certain concentrations. The mobility of heavy metals is dependent on pH and mechanisms such as ion exchange, sorption and desorption etc. The heavy metals can form precipitates with sulfide, carbonate or hydroxide in certain pH ranges (9). Esteves lists the heavy metals according to their relative toxicity as follows; Ni, Cu, Pb, Cd, Cr, Zn, Fe (from the highest to the lowest) (9).

The detrimental effects of accumulation of volatile acids are mostly observed on the population of methanogens, although some end-product repression may be observed for the acidogens (1). An increase in the volatile acids concentrations during anaerobic digestion can distrupt gas production of methanogenic bacteria by decreasing pH (9). Therefore the effects manifested are related to environmental conditions, particularly pH and buffer capacity (1). Inhibitory effects are not observed at total concentrations of acetic acid, propionic acid and butyric acid up to 6000 mg/l (13). In landfill environment, volatile acid concentrations will rarely reach levels where inhibitory effects on methane production will be expected (13).

Inhibition of anaerobic ecosystem by various organic compounds has been reported by various authors (13). It is also reported that fairly high concentrations of organic compounds are needed to inhibit the anaerobic system. Finite amounts of halogenated organic compounds can be detoxified in the landfill environments through reductive dehalogenation reactions (3). However, chloroform has been reported to be extremely toxic even at low concentrations such as 0.5 mg/l, and caused inhibition in many anaerobic treatment plants (3). Inhibition of methane formation in the landfill environment may appear where significant amounts of industrial waste have been disposed of in the site or in local macroenvironments with leaking chemical containers (13).

Sulfide is another compound which may be inhibitory to the anaerobic system in certain amounts. Sulfide may be introduced with the waste or may be generated by the reduction of sulfate. Even though sulfide concentrations from 50 to 100 mg/l of sulfide are tolerable for the anaerobic systems, concentrations above 200 mg/l terminate gas production.

Alkaline and alkaline-earth metals salts such as sodium, potassium, calcium and magnesium are also reported as toxic above threshold concentrations.

Esteves gives five possible control methods for inhibitory materials; removal of toxic materials from the waste, dilution of toxic materials, formation of insoluble complexes or precipitates, antagonizing toxicity with another material and pH adjustment (9).

2.2 Enhancement of Landfill Stabilization

It has been known that biological processes taking place in the landfill are responsible for the degradation of solid waste. It may take decades to achieve this stabilization and some authors believe that a landfill will not achieve a complete stabilization, in any reasonable time frame, without the optimization of conditions (16). Therefore, long-term emissions and reclamation of closed up landfills are the main problems in the area of sanitary landfilling. These problems can be solved if the period of stabilization can be shortened by enhancing anaerobic microbiological processes in the landfill.

Therefore, the perception of enhancing solid waste stabilization with various techniques is gaining importance in the management and operation of sanitary landfills. Enhancement of landfill stabilization has many advantages. First of all, enhancement of landfill stabilization is beneficial because of its effects on emission control and gas utilization. The enhancement of microbial activity promotes the transfer of the organic pollutant load from liquid to the gaseous phase which will result in lower leachate emission rates and higher gas production (15). This gas production will also be concentrated over a shorter period of time.

The other reason of enhancement of stabilization is the utilization of landfill gas which is collected to reduce environmental hazards. It can be used to generate electricity or heat.

Gas recovery rates for utilization are comparatively higher as a result of enhanced gas production.

When the enhancement of biological processes is achieved, the organic strength of leachate will be lower in the methane phase (because of the transfer of organic load to the gaseous phase) and the period when leachate is highly polluted is short therefore leachate treatment will be easier and less expensive (17) .

The success of a landfill management depends not only on operations but also the conditions of site after closure. Since the main gas production phase can be limited to a shorter period of time with enhancement, there would not be environmental nuisance in the closed-up landfills and reclamation of sites will be less problematic (14).
In addition to these, the long-term effectiveness of barrier systems are unknown; enhancement of activities helps earlier stabilization which result in less emissions of organics after decades when some barrier systems may be less effective (15).

2.2.1 Enhancement Techniques for Landfill Stabilization

The environmental factors such as moisture content, pH, nutrients that are most critical for anaerobic degradation in landfills are discussed in the previous sections. However, many of these factors can not be controlled individually in the landfills due to the rough and uncontrollable nature of landfill operations. Therefore, the actual management procedures are operationally defined and will simultaneously influence several of these factors.

There are several research activities on the effects of various landfill management options on landfill stabilization. The enhancement options can be listed as follows; leachate recirculation, pH control/buffer addition, nutrient addition, compaction, sludge addition, shredding etc. (18, 19). These techniques are described below;

Leachate Recirculation is one of the most popular landfill management options. It is practised by applying the leachate to the cell from which it originates. Leachate recirculation has been observed to enhance the methane production in landfills (22). As reported by Christensen, Kjeldsen and Stegmann, it increases the moisture distribution, establishes syntrophic microbial population and maintains conditions suitable for degradation and therefore accelerates solid waste stabilization (18).

The results of leachate recirculation studies, while differing on some conclusions, show that practicing leachate recycle had a positive effect on the solid waste stabilization (22). As an example Barlaz et al. concluded that leachate recycle stimulated the production of methane (10). Pohland and Onay reported in their study that the time required for the stabilization of solid waste was also decreased by this application (7).

pH Control/Buffer Addition; Christensen and Kjeldsen reported pH as the most critical parameter in obtaining an effective methanogenic degradation of the landfilled waste (18). In most of the research buffer addition has had positive effects on the degradation; only Stegmann and Spendlin (20) reported negative effects of pH adjustment by NaOH addition (18). pH control is established by adding a solid buffer materials such as calcium carbonate or adjusting the leachate before recirculation by addition of buffer solution (18). Buffer addition is especially required to establish methanogenic conditions if a landfill has failed to produce methane due to low pH values.

Nutrient Addition; addition of major nutrients such as nitrogen and phosphorus has been found to have positive effects on solid waste degradation. Leuscher found that the beneficial effects of additional nutrients are most clearly seen in the duration of lag period (21). Nutrient addition decreases the length of time for methane production to begin and increases the rate of stabilization during this time (21). Kinman et.al. also reported positive effects of nutrient addition on methane production (19).

Compaction; compaction may also affect anaerobic decomposition but there are not many experimental work done about these effects. Ing and Ehrig has come to the result that the refuse should be compacted in thin horizontal layers (this will intensify biological processes) at the site (4). One of the other studies at this subject concludes that the time of the compaction of the upper level may be seen as a possible control of acid phase and hence of the initiation of the methanogenic phase (18).

Sludge Addition, in spite of the many research work on the effects of sludge addition on anaerobic degradation, there is not a simple conclusion about these effects. There are studies resulted with positive effects, negative effects or no effect (18). But it may be concluded that anaerobically digested sludge gives positive results whereas negative effects are found for septic tank sludges (18). For example, Kinman et al.(19) observed the most enhanced methane production with anaerobically digested sludge addition. However Barlaz et al. (10) resulted that the use of anaerobically digested sewage sludge was not successful for anaerobic degradation.

Positive effects of this operation could be attributed to the increase in water content, supply of an active anaerobic biomass and readily available nutrients (18). The pH of the sludge is also important for its effect on degradation, it was observed that sludge low in pH (like septic sludges) has negative effects while well buffered sewage sludges may have positive effects (18).

Shredding; some of the reported investigation show a negative effect of shredding on waste degradation (18). It intensifies the acid formation eventually resulting in inhibition of methane production. However, there are also some studies concluding that shredding stimulated the rate of methane formation (28).

The well-mixed, shredded refuse permits greater contact between the key refuse constituents required for methane formation; moisture, substrate and microorganisms. Thus, a smaller particle size could result in an increase in the rate of hydrolysis, leading to a build-up of volatile organic acids and a lower pH. This may cause an inhibition in methane formation (28).

2.3 Codisposal of Solid Waste and Sludge

Although the primary objective of the study is to investigate the stabilization potential of solid waste, such a set-up also enables to study the effects of sludge addition to solid waste stabilization. Therefore this study may address to an alternative way of sludge disposal, namely landfilling of sludge.

The most common sludge disposal methods are incineration, land application, composting and landfilling. A large portion of the sludges can not be disposed by either incineration or land application due to rather high moisture content and low calorific value for incineration and low agricultural value and toxic materials content for land application. Therefore, landfilling of sludges is a common way of sludge disposal which also includes the disposal of the problematic sludges mentioned above.

Landfilling is a sludge disposal method in which the sludge is deposited in a dedicated area, alone or with solid waste, and buried beneath a soil cover (25). The sludge-only landfills are out of the scope of this study, therefore the codisposal sites of sludge and solid waste are described in this section.

Codisposal is defined as the receipt of sludge at a conventional landfill receiving municipal refuse (24). There are two methods of codisposal; sludge/refuse mixture and sludge/soil mixture. In the sludge/refuse mixture method, sludge is deposited on the top of refuse and then mixed and buried with the refuse. Most of the problems encountered at the codisposal sites are operational due to the liquid nature of sludge relative to solid waste; as a result of this nature sludge is difficult to confine at the working face, equipment slips and sometimes becomes stuck in the sludge while operating (24). The sludge received by the solid waste should not exceed the absorptive capacity of refuse in order to minimize these difficulties. The maximum allowable sludge quantity depends largely on the quantity of refuse received and the solids content of the sludge.

The advantages of codisposal can be expressed as follows; there is a shorter regulatory delay for sludge disposal at an existing landfill process than a sludge-only site and this method of disposal is more cost effective when compared to sludge-only disposal. However, codisposal has also some disadvantages such as operational problems, odors, sludge storage problems etc. In spite of these drawbacks, landfilling has been and continues to be a popular disposal option for sludges.

There has been many studies in the literature attempting to find out the effects of sludge addition on the solid waste degradation; both positive and negative effects were found in these studies. Some of the researchers reported that sludge addition increases the performance of anaerobic digestion. Potential positive effects of sludge addition to solid waste may be attributed to increasing water content, supply of an active anaerobic biomass and supply of readily available nutrients (18). Especially anaerobically digested sludge serves as a seed of microorganisms as well as a source of nitrogen, phosphorus and other nutrients (26).

Blakey et. al. concluded that codisposal of different kinds of sludge increase the rate of stabilization and increase the gas production (24). In this study, different sludge types (raw dewatered, liquid digested) were codisposed with the solid waste by different mixing strategies such as completely mixed, layered etc. in two different infiltration rates. The highest sludge:waste ratio used was 1:4.1 due to operational conditions. They concluded that gas generation and waste stabilization take place over a shorted time with sludge codisposal. Kinman has also obtained results supporting this conclusion (19).

Leuschner has reported that anaerobically digested sludge exhibited a significant beneficial effect upon degradation (21). In this study, several different additions such as buffer, sludge, nutrients were performed. The sludge added was 1.5% of the amount of solid waste in this study. It was concluded in this study that establishing a viable population of microorganisms in the reactor significantly increased the rate of methane formation.

Buivid et. al. have also observed the positive effects of digested sludge addition on waste degradation (27). These positive effects were again attributed to the supply of nutrients and active population of methane-producing bacteria. It was stated that these bacteria were spore-forming; they could exist in a suspended state until the proper conditions were available for activation (27).

These positive effects were most of the time observed at neutral or well-buffered sludges, showing that the pH of the sludge plays an important role on its effect. Barlaz et al. (10) found that anaerobic sludge addition without buffer addition did not stimulate stabilization and methane production. Supporting this idea, some researchers found that the addition of septic tank sludges with low pH values stimulated acid production and inhibited methane formation due to a pH decrease. Besides the importance of pH, some researchers suggest that the sewage sludge addition may have a limiting effect on waste degradation if the anaerobic environment is already established (18).

When environmental aspects of sludge landfilling are considered, it is necessary to know the effects of sludge on the disposed waste. Therefore solid waste studies with sludge addition are important for determining these effects. These studies are also important for the minimization of the problems encountered in codisposal of solid waste and sludge.

2.4 Methane Production in Landfills

The primary landfill gases can be listed as follows; methane (CH_4), carbon dioxide (CO_2), hydrogen (H_2), nitrogen (N_2), carbon monoxide (CO), hidrogensulfide (H_2S), oxygen (O_2) and other trace compounds (30).

The landfill gas constitutes a potential hazard in six ways; air depletion in soils may cause damage to vegetation, the built-up of flammable and explosive concentrations of methane rich gas, landfill gas leakage, damage by settlement, the creation of odour and potential health risk and water pollution (30).

The objective of this section is to focus on the production of methane in the landfills because it is the main component of the landfill gas that causes the listed potential hazards and it can also be utilized as a source of energy. It also constitutes 70 % of the landfill gas with carbon dioxide; trace compounds making up the balance (5).

Methane is a colorless, odourless gas which can be found where organic decomposition takes place in anaerobic conditions such as landfills. It is soluble in water and lighter than air. Methane concentrations from 5% to 15% in the air can explode with a source of ignition under suitable conditions. It is not toxic to the plants but can cause depletion of oxygen in the soil (5).

2.4.1 Theoretical Methane Yield of Solid Waste

Knowledge of landfill gas quality and quantity is an indicator parameter of degree of landfill stabilization and it is obviously important in evaluating the potential for gas production and migration. It is also important in assessing the feasibility of a gas recovery system (32).

There are basically two methods for the estimation of theoretical maximum yield of methane from municipal landfills (5). These are methodologies employing the basic stoichiometry of the conversion process and utilization of an assumed conversion efficiency.

The stoichiometric method is based on an empirical formula representing the chemical composition of solid waste and the overall process stoichiometry approximating the combined mechanisms which take place during anaerobic decomposition of the refuse (5). There are a number of similar formulas used for this method; one of the most popular ones is given below as the Equation 1 (32);

$$C_nH_aO_bN_c + [n - (a/4) - (b/2) + 3(c/4)]\ H_2O \longrightarrow [(n/2) - (a/8) + (b/4) + 3(c/8)]\ CO_2 + [(n/2) + (a/8) - (b/4) - 3(c/8)]\ CH_4 + cNH_3$$

The representative chemical formula of the solid waste is used in the reaction to determine the maximum potential methane yield. This method does not include any evaluation of the extent of biodegradability of the organic matter, only the basic chemical composition of the solid waste to be known (5). The research studies given as references at Emcon Associates (1980), Laquidara & Leuschner (1987), Barlaz & Ham (1989) used this approach for the determination of the gas generation potential of the municipal solid waste (5, 33, 31).

Another approach is based on the overall biodegradability of the composite refuse. In this approach some of the necessary assumptions are made with the help of stoichiometry. Different methane yields were found in researchs with different assumptions of moisture content, the extent of biodegradability etc. An example of this approach is given in the work of Nynns and Gendebien (30). This estimation is given as follows;

The survey made by the researchers gave the following figures for an average municipal solid waste; 35% of moisture content, 75% of degradable organic matter on dry matter and a specific COD value of 1.2 gr COD per gr dry organic matter. When these figures are taken into consideration, the yield is expressed as below;

1 tonne of municipal solid waste=

$$10^6 \text{ gr} \times (1-0.35)\,\frac{\text{g dry weight}}{\text{g wet weight}} \times 0.75\,\frac{\text{g organic weight}}{\text{g dry weight}} \times 1.2\,\frac{\text{g COD}}{\text{g organic matter}} = 0.585 \times 10^6 \text{ g COD}$$

An assumption is made at this point from a theoretical relation between COD and methane;

$$1 \text{ gr COD}_{\text{organic matter}} = 0.35 \text{ l } CH_4 \quad \text{at } 0\ ^{\circ}\text{C and 1 bar}$$

By using this assumption;

$$Y_{\text{methane/kg solid waste}} = 0.585 \times 10^6 \text{ g COD} \times \frac{0.35 \text{ lt } CH4}{\text{gr COD}_{\text{organic matter}}} = 205 \text{ l/ kg municipal solid waste}$$

These theoretical models and the available data from researchs are the important tools for the prediction of total gas generation. The best data is likely to come from landfills and full scale gas utilization projects. However, there is little data from landfills because of the long period of monitoring required and also because of difficulties of measurement; in addition to these the data from gas utilization projects might be available in the next several years (32).

Ham and Barlaz stated that it was difficult to project the total quantity gas to be obtained in a full-scale landfill from theoretical considerations alone (32). This is due to competing reactions and resistant materials which will not form methane. The authors give the total amount of methane to be formed in a full-scale landfill in the range of 50 - 124 l CH_4/kg solid waste, taking the various measurements into account from different types of experiments (32). The Emcon Associates also give the total methane production in the range of 31 to 94 l CH_4/kg solid waste for conditions prevailing in most sanitary landfills (2).

2.5 Determination of the Remaining Stabilization Potential in Landfills

Determination of the stabilization potential of solid waste and the degree of stabilization at the site play important roles for the efficient landfill management. The degree and rate of stabilization in a landfill can be a valuable parameter for future predictions of leachate and gas generation and differential settlement.

Researcher followed different approaches for this determination. Chemical analyses and mass balances were used for assessment of the degree of stabilization and maximum remaining methane potential (28). Some of these researchs are given below;

Bookter and Ham were the first to measure cellulose and lignin concentrations in landfills and they found the cellulose-to-lignin ratio as a useful index of the degree of stabilization and remaining stabilization potential (28). In this study, the volatile content was used as a measure of the total organic content of the refuse, and the cellulose and lignin were specific organic materials chosen for analysis because they occur simultaneously in nature and should be present in fresh refuse at a more predictable ratio than other candidate organic materials (35). After test lysimeter and operating sanitary landfill analysis; it was found that the volatile and cellulose contents decreased and the lignin content increased. Therefore, the cellulose to lignin ratio was found to be decreasing with the age of the landfill. It was suggested that useful information about the state of decomposition, decomposition rates and variables affecting decomposition can be obtained by this technique (35). However, the methane potential of the solid waste was not investigated in this research.

In his research, Laquidara proposed the estimation of the methane potential of landfill based on measurements on total solids, total volatile solids, total carbon and lignin concentrations in the solid waste (28). Stoichiometric results were used for the estimation of total methane production. It was concluded that if properly conducted, feasibility studies can accurately determine the potential gas production capacities in existing landfills (33).

Barlaz &Ham studied the methane production potential of the refuse by mass balances analysis (31). In this study, the decomposition of shredded municipal solid waste was studied under laboratory conditions with leachate recycle and neutralization (31). The chemical composition data and the mass balances were used to identify the principal degradable constituents of refuse and to estimate its methane potential (31). Gas volume and composition analysis and cellulose, hemicellulose and soluble sugar measurements were performed for the solid waste samples. In this work, carbon recoveries of 70 to 100% were obtained. It was concluded that the maximum cellulose plus hemicellulose degradation can be used to project methane yields from landfills by using the mass balances (31).

Pohland et. al. also studied on the determination of remaining stabilization of landfilled solid waste after exposure to leachate recirculation. In this research, the anaerobic degradation of solid waste was enhanced with various techniques such as pH control and/or nutrient addition, sludge addition to determine the existing degree of stabilization and potential to produce additional methane gas. Theoretical methane yield of 200 to 500 l CH_4/kg solid waste was compared with the actual yield in this study for the determination of remaining stabilization potential (34).

A method for the analysis of the degree of refuse stability in a landfill has many beneficial practical applications such as prediction of the future leachate and gas generation, determination of the feasibility of a landfill methane recovery program, evaluation of the closure time and the final use of the site, determination of the gas migration potential.

3. MATERIALS AND METHODS

In this study, further stabilization of landfilled solid waste is analyzed by the addition of anaerobically digested sludge to the solid waste with different ratios. The experimental part of this study consisted of anaerobic digestion of landfilled municipal solid waste with sludge addition.

Four reactors were placed into a constant temperature aquarium at an average temperature of 34 °C. These reactors were operated with different sludge to waste ratios in order to find the optimum ratio for methane formation and also to determine the effects of sludge addition on solid waste degradation.

Solid waste samples used in the reactors were taken from an operating landfill; İzmit-IZAYDAŞ. The anaerobically digested sludge that was used for the enhancement of stabilization was obtained from the anaerobic wastewater treatment system of a liquor factory of TEKEL. A physical and chemical solid waste and sludge characterization were performed prior to the commencement of reactor operations.

IZAYDAŞ from where the solid waste was taken is owned by Izmit Municipality. It consisted of Hazardous and Medical Waste Incineration Facility, Izmit Municipal and Industrial Wastewater Treatment Plant and Industrial and Municipal Solid Waste Landfill (40).

Industrial and Municipal Solid Waste Landfill is made up of six municipal solid waste disposal area with a total capacity of 3.125.000 m^3 and one disposal area for industrial waste with 790.000 m^3 disposal capacity. The approximate life of the landfill was estimated as 25 to 30 years (40). The solid waste used in the experiments was taken from one of the municipal disposal area of the landfill.

3.1 Analysis of Solid Waste and Sludge Used in the Experiments

Solid waste was retrieved from approximately 1.5-2 m depth. The retrieved solid waste was put into big plastic bags after separating large plastic fragments, metals, large glass fragments and diapers etc. These bags were stored in cold room at a temperature of 4 °C until they were separated again, tested and used.

Four 2 kg solid waste bags were prepared from the separated portion. After samples were taken from these bags for heavy metal determination, bags were stored at the cold room at 4 °C until the reactor loading and they were again inspected for metal particles at the time of loading. The following analyses were performed prior to the loading of the reactors.

3.1.1 Moisture Content Analysis

Approximately equal amounts of solid waste were taken from different parts of the bags in order to obtain representative samples. After weighing these samples, they were placed in 103 °C for 24 hours. The samples were then removed and reweighed after they were cooled in the desiccator. The moisture content of each sample was calculated as the weight difference of the samples before and after heating. The same procedure was used for the determination of the moisture content of the sludge (41).

3.1.2 Heavy Metal Analysis

It is known that the heavy metals at concentrations above threshold values may be inhibitory to the system. Therefore, the heavy metal analyses were performed in order to detect a possible inhibition of the metals.

These analyses were not performed in the laboratory of the Institute. After solid waste was separated at the laboratory, four 2 kg bags were prepared for loading and four samples were taken from every bag for heavy metal determination. These samples were brought to IZAYDAS for the analysis. The analysis was performed by ICP after acid digestion step at the laboratory of IZAYDAŞ.

It should also be noted that before the retrieved solid waste was loaded, it was again inspected in order to separate any visible metal particles like coins, rods etc. however the samples given for the analysis were taken from the bags before this separation. Therefore the heavy metal concentrations in the solid waste used for the study is probably lower than the results of the heavy metal analysis.

3.1.3 pH Analysis

The researches on the codisposal of sludge and solid waste show that the pH of the sludge is primarily important for the effects of sludge on the solid waste stabilization. Therefore the pH of the sludge was measured prior to loading. pH of the leachate samples was measured by WTW pH-320.

3.2 Preparation of the Anaerobic Reactors

3.2.1 Configuration of the Reactor System

Four 10 lt. plexyglass reactors were prepared and placed in a plexyglass aquarium in order to keep the system at constant temperature. Each reactor had a diameter of 20 cm and a height of 30 cm. The aquarium was prepared with a base of 100x 30 cm and with a height of 40 cm.

The reactors had a sloped outlet near to the bottom of the reactor in order to take leachate samples. They also had a port with a V-shaped connection at the top of the reactors that is connected to the gas collection system in order to collect the generated gas, the other opening of the port could be used to take gas samples and to add liquid if necessary. The system configuration is given in Figure 3.1

The generated gas was collected and measured by inverted glass cylinder method. A 0.5 lt glass cylinder was inverted and placed into a 1 lt cylinder which was filled with confining solution. The inner cylinder was lifted until the levels of confining solution at both cylinders equilibrated and the amount of gas generated was indicated by the volume occupied in the inner cylinder (3).

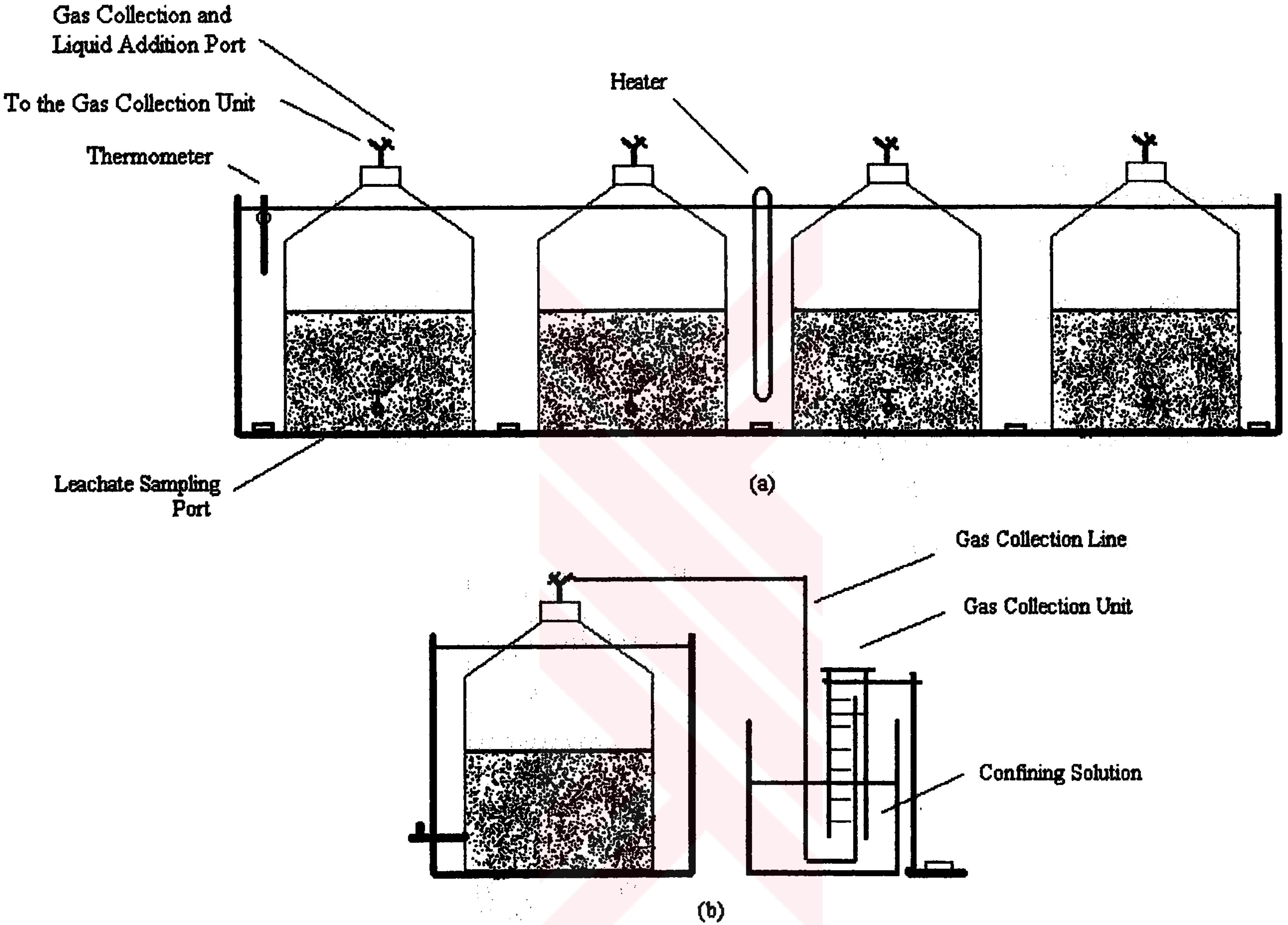

Figure 3.1. Configuration of the Reactor System

(a) Plan View
(b) Side View

The confining solution was prepared according to Standard Methods No. 2720.B (41). A sodium sulfate-sulfuric acid solution was prepared in order to confine carbon dioxide and methane.

The reactors were tested against any gas or liquid leakage before loading; the system was closed and sealed with silicone as it is loaded and remained pressurized for 24 hours in order to observe any leakage. Leak test was conducted until no leakage was observed at the reactors.

After the experiments started, it was observed that the gas production exceeded the capacities of the cylinders for collection. This brought difficulties in observing the real gas production at the reactors. Therefore, a modification was made in the gas collection system after the first week of operation. A smaller aquarium was partially filled with the confining solution. One liter plastic cylinders were placed in the aquarium in a converted position and they were filled with the solution in this position.

The system worked with the same principle; the generated gas was replacing the solution in the cylinder and the generated gas was indicated with the water level at the cylinders. It was possible to place only four cylinders into the aquarium. The reactor with the highest gas generation was connected to two cylinders and the gas collection capacity of this reactor was upgraded to two liters. Each of the two other reactors were connected to one cylinder and reached to one liter of gas collection capacity. The old gas collection unit was kept for the control reactor, but one extra cylinder was added to the gas collection unit. It was aimed to maximize the gas collection capacity for each reactor.

3.2.2 Loading of the Anaerobic Reactors

Four reactors were planned for the study. Different sludge:waste ratios were selected for these reactors prior to loading of the system. Each parameter other than sludge:waste ratio was kept approximately equal for every reactor except the solid waste composition. It was not possible to control waste composition because landfilled solid waste was used for the study.

The moisture contents of the reactors were selected as 85 % because it was an anaerobic digestion study and the digestion is efficient at high moisture contents (34). This study was an optimization study other than a simulation one. Therefore, moisture content should be higher than 80 % for maximum decomposition and it was selected as 85 % (34).

In order to make the sludge:waste ratio estimation, the weight of the solid waste to be put in the reactors was initially calculated. When the volume of the reactors and the amount of water required to obtain the selected moisture content were considered, it was concluded that 1,5 kg of waste should be loaded to every reactor.

This selected value is also advantageous for the mixing of the reactors. In conventional digestion, stirring brings the substrate into content with the microorganisms and therefore important for the efficiency of operation (28). It was not possible to use a stirring apparatus in this study due to the use of a large aquarium full of water for temperature control. Therefore, the reactors were shaked manually every day. If the reactors were totally full, it would not be convenient to mix them in this way.

After the selection of the amount of solid waste in the reactors based on the capacity of the reactors; the sludge:waste ratios were selected. One of the reactors was loaded only with solid waste without any sludge addition and this reactor was called "Control Reactor". The other extreme point; the highest sludge to waste ratio was selected according to the design considerations for codisposal operations. In the EPA Report of "Municipal Sludge Landfill", the bulking ratio for the sludge solids content of the sludge used at the study was given as 4 tons of refuse:1 wet ton sludge (23). In addition to this information, Craft and Blakey gave the highest sludge to waste ratio to be adopted in operational practices as 1:4.1 (24). Therefore, the highest sludge to waste ratio was selected as 1:4 in this study.

After the determination of the lowest and highest sludge:waste ratios as 0 and 1:4 respectively; two other values were selected in between these ratios as 1:9 and 1:6. If these ratios were converted to percentages, the sludge percents of the reactors may be given as follows; 0 %, 10 %, 14% and 20 %. The ratios in between were selected closer to the upper limit due to the fact that the range near to the upper limit was more critical than the range lower than 10 %. It was due to one of the objectives of the study, namely the investigation of a possible sludge disposal option. To increase this ratio seemed beneficial for this objective due to the increased amount of sludge to be disposed. However it was also known that the quantity of sludge should not exceed the absorptive capacity of the refuse at the site. Therefore the risk of exceeding absorptive capacity of solid waste increases with the increasing ratios. As a result, the upper range seemed critical and the ratios were selected within this range. The amounts of solid waste and sludge loaded to the reactors are given in Table 3.1;

Table 3.1. Loading Conditions of the Reactors

Reactor	Sludge:Waste Ratio	Moisture Content	Solid Waste Added-Wet (gr)	Sludge Added-Wet (gr)	Water Added (lt)
1	0	85%	1500	-	4
2	1:9	85%	1500	166	4,054
3	1:6	85%	1500	250	4,083
4	1:4	85%	1500	375	4,125

The amount of water to be added to each reactor was calculated by using the moisture contents of sludge and solid waste and adjusting the moisture content of the system to 85% (by using these values).

On the day of the loading of the reactors; the stored solid waste and sludge was taken out of cold room to ambient temperature, then the reactors were loaded according to the values given in Table 3.1. After the process of the loading of the components, each reactor was carefully stirred and then sealed with rubber stopper and silicone around the stopper. The reactors were also purged with helium gas to displace air form reactor headspaces to obtain anaerobic conditions and then the aquarium was filled with hot water.

3.2.3 Reactor Operations

Throughout the study, the water temperature at the aquarium was kept constant at 34 °C. All reactors were operated in the batch mode without leachate recirculation.

The system worked without any addition of water and pH adjustment except 20th day of the operations. On Day 20, 250 ml of water was added to the reactors due to a sudden decrease in gas production in order to see if this decrease was related to moisture lost until that day. This addition was also made due to a sharp pH decrease in the Control Reactor.

3.3 Analysis of the Leachate From the Reactors

Leachate samples collected from the outlet near to the bottom of the reactors were analyzed for pH, ORP (Oxidation-Reduction Potential), COD (Chemical Oxygen Demand), orthophosphate, ammonia nitrogen, chlorine and alkalinity. All these analyses were performed according to "Standard Methods for the Examination of Water and Wastewaters" (41) and briefly explained below, the frequency and methods of these analysis are given in Table 3.2. The frequencies of the analysis changed during the stabilization.

Table 3.2. Methods and Frequency of Leachate Analyses

Measurement	Method (Standard Methods for Water and Wastewater) (41)	Frequency
PH	Examination # 2730.B	Every Day
ORP	Examination # 2580	Every Day
COD	Examination # 5220 D	Every Day
Ammonia Nitrogen	Examination # 4500- NH_3 E	Twice a Week
Orthophosphate	Examination # 4500-P E	Every 2 Weeks
Chlorine	Examination #408 A	Every Week
Alkalinity	Examination # 2320 B	Every Month

pH and ORP are physical-chemical parameters which were monitored for the indication of acid-base conditions and for oxidation-reduction monitoring, respectively (1). pH of the leachate samples was measured by WTW pH-320 and the ORP was measured by a ORP probe attached to a model SAS20 pH meter.

COD is an important parameter observed for the determination of the organic strength of leachate. COD analysis was performed by the dichromate closed reflux method. In these experiments, samples were prepared by pipetting them into COD vials with potassium dichromate and sulfuric acid digestion solution. These vials were kept at 150 °C in Hach COD Digester for 2 hours. After this step, the absorbances were measured by Hach DR/3 Spectrometer. The COD results were obtained by plotting the absorbances on the calibration curve prepared by a standard KHP solution.

Ammonia Nitrogen was determined by preliminary distillation method followed by titrimetric method. Preliminary distillation was performed by Gerhardt Vapodest Distillation Apparatus. The samples were buffered to approximately pH 9.5 and then distilled into boric acid solution for 15 minutes. Following the distillation step, the distillates were titrated with standard sulfuric acid (0.2 N) for ammonia determination.

Orthophosphate present in the leachate were determined by the Ascorbic Acid Method. A combined reagent was prepared with sulfuric acid, potassium antimonyl tartrate solution, ammonium molydate solution and ascorbic acid. This reagent was added to samples and the absorbance of the sample was measured at 880 nm after color development. The orthophosphate concentrations were determined by using a calibration curve drawn with the phosphate concentrations of a series of standard phosphate solutions which were determined by the same method.

Chloride was also measured to monitor the effect of dilution in the leachate samples. This analysis was performed by Argentrometric Method where the sample was titrated by silver nitrate ($AgNO_3$). The end point of titration was detected by potassium chromate indicator.

3.4 Analysis of the Gas from the Reactors

The gas generated in the reactors were monitored for the understanding and identification of the stabilization phase of the solid waste in the system. The volume of daily gas production and the gas composition were the monitored throughout the study.

The gas production was measured daily by observing the displacement of the confining solution at every gas collection unit. This production was determined every day after the shaking of each reactor. When the capacity of gas collection units were exceeded, the generated gas was vented to open air through one of the openings of V-shaped port without allowing any air intrusion to the reactors.

The gas composition analyses were performed at Istanbul Technical University (ITU) Department of Chemical Engineering. The analysis started at 24.11.1998 on the Day 33 day of the study due to some difficulties in carrying the samples to ITU. The samples were tried to be carried with different methods in order to prevent escaping of sample contents before injection. After a period, it was concluded that carrying samples in 10 ml glass sampling bottles gave the best results. The samples were carried by this way until the end of the study. Although these bottles gave the best results, some of the samples were lost on some of the analysis days.

The generated gas composition was analyzed once in ten days. The gas composition analysis was performed with a HP 5890A Gas Chromotography with nitrogen gas as a carrier. Carbon dioxide (CO_2) and methane (CH_4) percentage in the injected sample were determined.

The oven temperature of the GC was programmed to operate at 70 °C for every run and the final temperature was 150 °C. Gas Standards for methane and carbondioxide were used to calibrate the equipment and to obtain the calibration curves for these gases. A HP Integrator recorded and printed the peaks of the present gases in the sample. The percentages of the gases in the sample was calculated by plotting the areas under the peaks to the calibration curves.

4. RESULTS AND DISCUSSION

4.1 Analysis of Solid Waste and Sludge Used in the Study

The results of the analysis of the solid waste and sludge used in the study are given below.

4.1.1 Moisture Analysis

Moisture analysis of solid waste was performed with four equivalent amount samples taken from different locations of the storage bags. The overall moisture content was taken as the average of these samples plus the moisture content determined with the sample left at IZAYDAŞ for analysis. After this determination, 45 % was taken as the overall moisture content of solid waste. The moisture content of sludge was determined as 20 % by the same approach.
These values are given in Table 4.1.

The estimated moisture contents were used to determine the amounts of water to be added to each reactor in order to adjust the moisture contents to 85 %.

Table 4.1. Moisture Contents of Solid Waste and Sludge Used in the Study

Sample	Solid Waste	Sludge
Sample 1	50.65 %	23.41 %
Sample 2	40.32 %	18.75 %
Sample 3	43.36 %	20.1 %
Sample 4	42.14 %	
Sample 5 (IZAYDAŞ)	57.6 %	
Overall Moisture Content	45 %	20 %

4.1.2 Heavy Metal Analysis

The heavy metal analyses of the solid waste samples were performed in order to detect a possible heavy metal inhibition in the systems. The results of the analysis were compared with the European Council limit values (26).

Esteves lists the heavy metals according to their relative toxicity as Ni, Cu, Pb, Cd, Cr, Zn, Fe from the highest to the lowest (9). The solid waste samples were analyzed for the eight heavy metals at the laboratory of IZAYDAŞ. The results of the analysis are given in Table 4.2.

Table 4.2. Heavy Metal Concentrations in Solid Waste Samples

Parameter	Concentrations (g/ton)				
	Sample 1	Sample 2	Sample 3	Sample 4	Limit Values
Nickel	225.88	183.08	203.61	158.61	400
Copper	617.83	377.46	539.47	677.24	1750
Lead	1283.03	1550.76	1176.08	4789.36	1200
Cadmium	<3.12	<2.69	<3.19	<3.20	40
Chromium	595.71	307.73	500.57	408.14	1500
Zinc	5496.01	3238.83	5690.8	6240.59	4000
Arsenic	56.8	35.86	72.97	40.81	-
Mercury	<1.87	<1.62	<1.91	<4.71	1500

Among eight heavy metals examined, nickel, copper, cadmium, chromium, mercury and arsenic were found to be much lower than the limit values. Lead concentrations were found to be close to the limit value except the fourth sample which was much higher than this value. Same problem appeared also in zinc analysis where zinc concentrations of all samples were higher than the limit value. Among these four bags from which these samples were taken, only the fourth bag was not used due to high concentration of lead. High zinc concentrations in all samples were not taken into account due to its relatively low inhibition potential.

It is also a fact that the solid waste bags analyzed for heavy metals were also inspected at the time of loading. Therefore, the heavy metal concentrations in the reactors were lower than the results of this analysis. As a result, heavy metal inhibition was not expected in the reactors and therefore the solid waste taken from the site was loaded to the system.

4.1.3 pH Analysis

pH of the sludge was measured after it was taken from the treatment plant. It was measured as 6.9. Two more samples from the same treatment plant were taken and analyzed in two different times. The pH's of these samples were 6.8 and 7.1, respectively.

As understood from these values, the sludge used for the study was a neutral sludge.

4.2 Analysis of the Leachate from the Reactors

4.2.1 pH

The pH of the waste environment is given to be the most critical parameter in an effective degradation of the landfilled waste by Christensen and Kjeldsen (13). pH is dependent upon interaction between volatile organic acids and alkalinity in the leachate and also the partial pressure of generated carbon dioxide gas (3, 8).

Maintenance of pH within an acceptable range is essential for the anaerobic degradation (1). In general, acid forming bacteria have an optimum pH range of 5-6. Methanogens have a higher optimum range that this range; methane formation will proceed in a pH range of 6.5 to 8.0, the optimum pH for methane generation is between 7.0 to 7.2 (2). As Pohland et. al. stated, these acceptable ranges of pH are primarily controlled by bicarbonate buffering capacity that is measured in terms of alkalinity (1).

During the acid formation phase, an accumulation of organic acids accompanied by a reduction in pH is observed. When the volatile organic acids are converted to methane and carbon dioxide by methanogens, pH begins to rise. Stegmann and Spendlin found that the pH increases automatically when the methane production starts (14).

The pH values of the leachates from four reactors are presented in Figure 4.1. It was observed that leachates of the three reactors with sludge addition (Reactor 2, Reactor 3, Reactor 4) exhibited a similar trend in the first 30 days of the experiments. The pH values of the leachates were within 7.2- 8.5 range in these reactors. Although the initial pH the control reactor (Reactor 1) was similar to the other reactors, it exhibited a different trend during 30 days. pH gradually decreased for 19 days until 5.78 in this reactor and a rapid increase was observed for 6 days to pH value 7.0 after the Day 19. This increase continued until pH 8 on the Day 27 and the Control Reactor came to the pH values similar to the other ones after this day.

After the Day 27, all four reactors exhibited a similar trend and stayed more or less constant until the Day 90 of the experiments. The pH values of the reactors were observed to be in 7.1- 8.1 range with a few exceptions and most of the days with a small deviation from 7.5. After the Day 90, a slight increase was observed for every reactor in 7.5-8.0 range with a maximum and minimum of 8.13 and 7.33, respectively. This increase was attributed to the drastic decrease of volatile acids in the reactor systems at the last weeks of the stabilization.

The pH values of all reactors exhibit a similar trend throughout the study. The most obvious deviation from this trend was the pH decrease until 5.78 that was observed at Control Reactor in the first 30 days. If the organic acid determination was performed in these days, an extensive organic acid accumulation might have been observed. An extensive COD release and an increase in gas production that were observed within this period were the indicators of this accumulation. This could be concluded due to the fact that the majority of COD is composed of VOA during the Acid Formation Phase.

This problem may be addressed as a souring problem. Souring occurs when the organic acids are produced by acid forming bacteria more rapidly than they are converted to methane and carbon dioxide (27). When this occurs, the pH drops, the methane bacteria are inhibited and methane formation ceases (27).

An evident of this explanation may be the sharp decrease of COD in the Control reactor that started after the Day 22 when the pH values increased to 7-8. This change may be

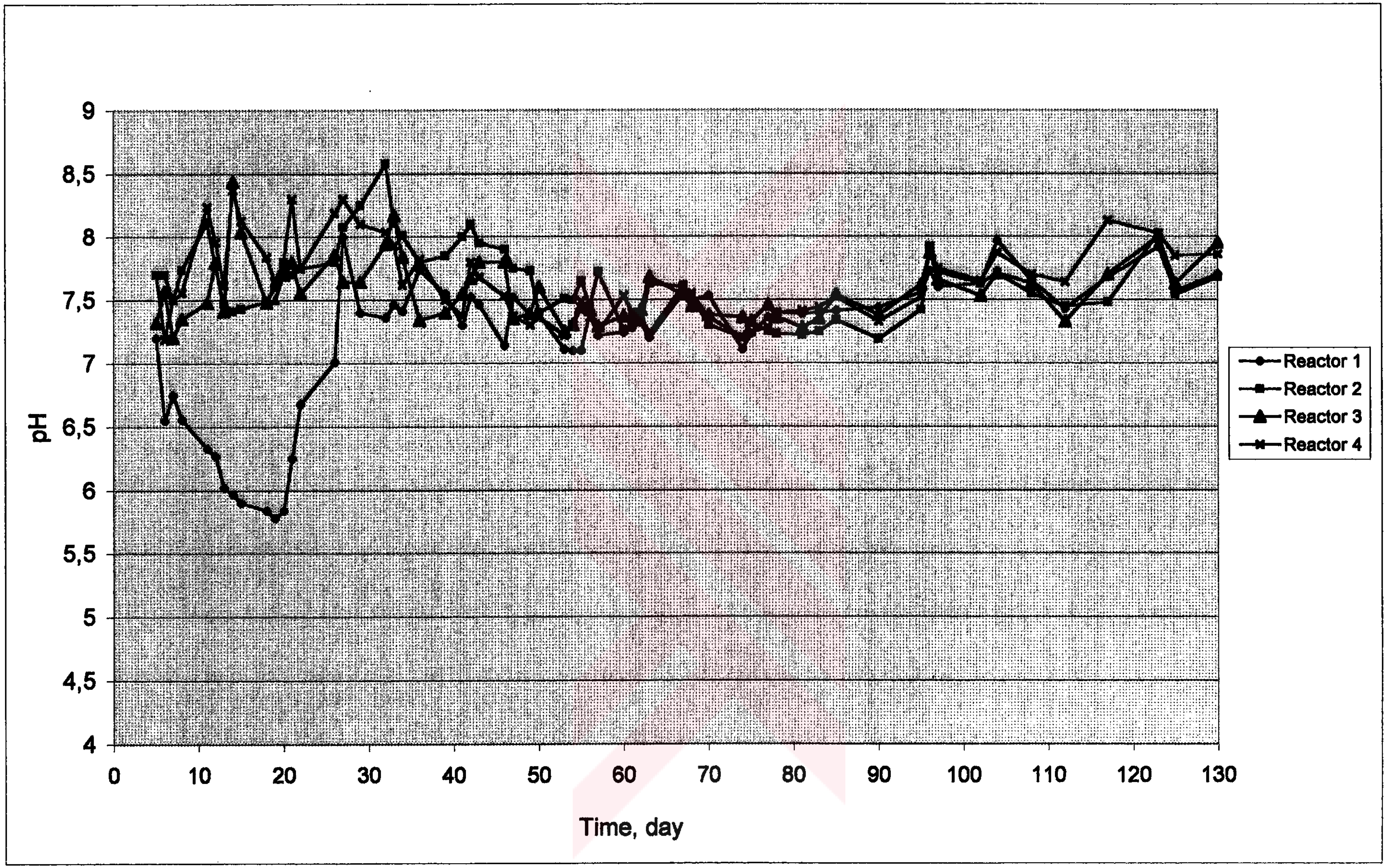

Figure 4.1. pH of the Leachate from the Reactors

attributed to 250 ml water addition on the Day 20 of the experiments. This water addition probably caused a dilution in the Control Reactor. By providing an improved environment through water addition, a viable population of anaerobic organisms became established in the reactor which enhances the decomposition of solid waste.

A similar problem was not observed in the reactors with sludge addition due to the fact that an active anaerobic biomass and necessary nutrients were supplied to these reactors with sludge addition. The buffer capacities of the systems were increased due to the sludge addition. Therefore, the conversion of organic acids to methane was possible in these reactors. It is also due to the fact that sludge added was a neutral sludge. Therefore, the release of organic acids that was reflected with the increase in the COD concentration was assimilated by the methanogens in these reactors.

Barlaz et al. found that acids accumulate and the pH decreases due to an imbalance between fermentative and methanogenic activity (28). It was also stated that the use of sludge to prevent the initial pH decrease was studied by many researchers to bring fermentative and methanogenic activity into balance (28). This is why an initial pH decrease was not observed at the reactor with sludge addition.

pH is also an important parameter that reflects the class of microorganisms active in the system. In general, acid forming bacteria have an optimum pH range of 5-6. Methanogens have a higher optimum range that this range, methane formation will proceed in a pH range of 6.5 to 8.0, the optimum pH for methane generation is between 7 to 7.2 (2). These given ranges support the souring and COD removal after souring explanations because they are the ranges in which the acid formers and methanogens were assumed to be active.

4.2.2 ORP (Oxidation-Reduction Potential)

Oxidation-reduction potential (ORP) was measured to understand the oxidizing or reducing condition states in the reactors throughout the study. The ORP measurements started at the Day 15 of the study. Measured ORP values for four reactors are presented in Figure 4.2.

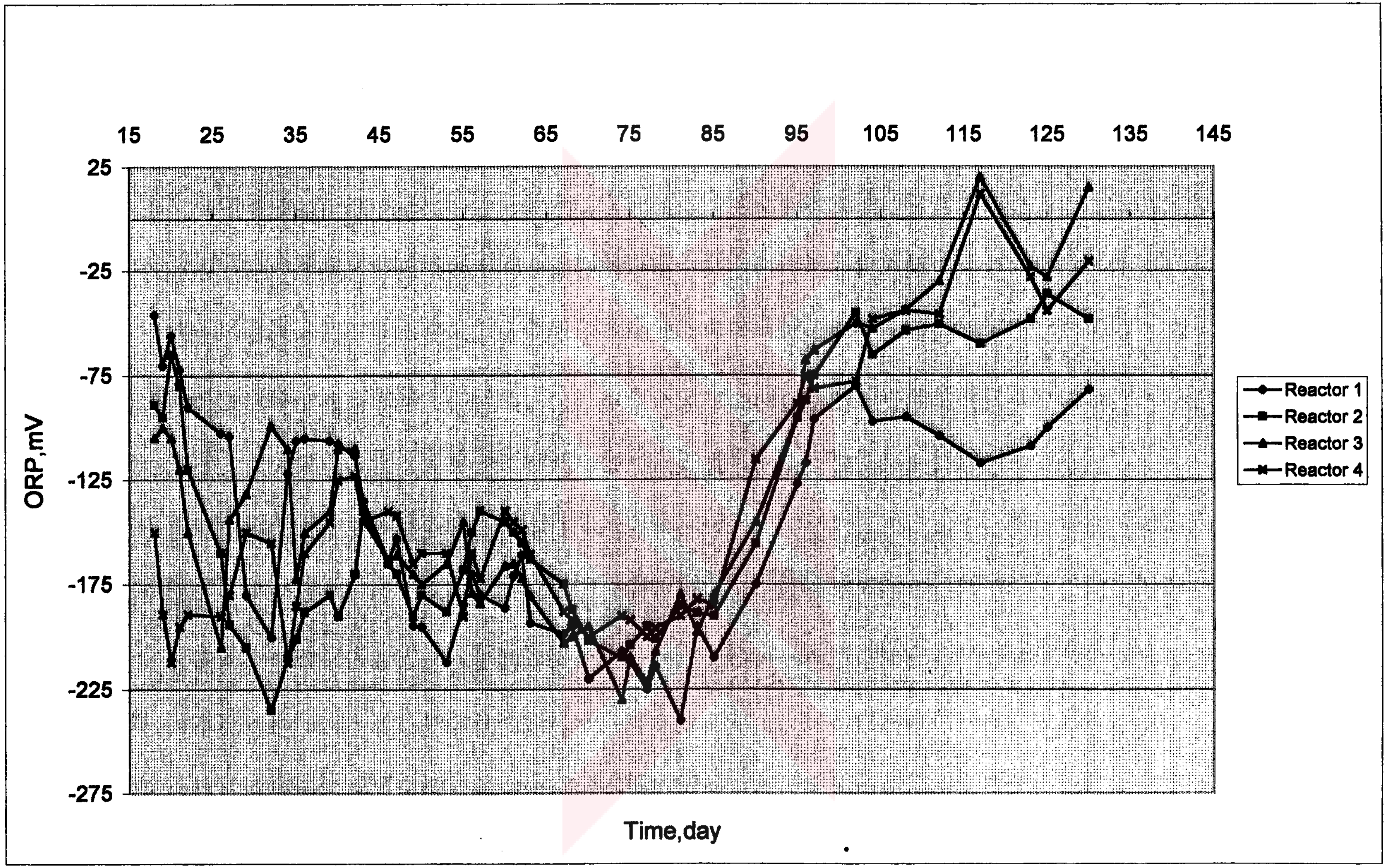

Figure 4.2. ORP of the Leachate from the Reactors

Initial ORP values in the reactors ranged from -46 to -150 mV. Negative values indicated that reducing conditions were being established in the reactors. The lowest ORP value was measured at Reactor 4 which was loaded with the highest sludge:waste ratio. The initial ORP values were observed to be decreasing with the sludge:waste ratios at the reactors, the highest ORP of -46 mV at Control Reactor. Therefore, it may be concluded that the addition of anaerobically digested sludge was beneficial for the establishment of reducing conditions at the start-up period.

Sharp declines of all ORP values were observed in all reactors except Control Reactor after the first 30 days. A different trend was seen at the Control Reactor, the ORP values decreased for few days and then stayed constant until the Day 27. On this day a very sharp decrease was observed at this reactor; the ORP decreased to -180 from -104 mV.

The period that the ORP values showed a sharp decline was also the one where an extensive COD removal took place in the reactor. This supports the fact that highly reducing condition is a prerequisite for the efficiency of methanogenic activity (3).

Between the Day 30 and Day 80 of the study, some fluctuations were observed in the ORP values of all reactors; but these fluctuations remained in the -125 to -225 mV range for each reactor. There were not very clear differences in ORP values between the reactors during this period. However, when the ORP trends of the Control Reactor and Reactor 4 were to be compared, they were the lowest and the highest respectively. This may be due to the fact that Reactor 4 had already completed the major portion of its decomposition at this time as the COD data showed. Unlike Reactor 4, Control Reactor which started anaerobic decomposition later was still experiencing decomposition.

After the Day 80, the ORP values started to increase to initial values in every reactor. Even positive ORP values were found in Reactor 3 and 4 on the Day 117. Furthermore, COD removal and gas production were very low during this period. All these observations were supporting to each other and as a conclusion, anaerobic decomposition of readily degradable organics was about to be completed in each reactor.

4.2.3 Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) was the only parameter monitored as an indicator of the organic strength. COD measurements started at the Day 6 of the experiments. The initial COD values were determined from the first day samples stored according to Standard Methods (41). The COD data for four reactors are presented in Figure 4.3 and 4.4.

The initial COD of the Control Reactor was much higher than the COD values of other three reactors. Initial COD values for the reactors are given as follows; Reactor 1, 7890 mg/l; Reactor 2, 2384 mg/l; Reactor 3, 1403 mg/l and Reactor 4, 1830 mg/l. The similarities of the initial COD values of Reactor 2, 3 and 4 suggested that the waste loaded to these three reactors was similar in composition. However the initial COD of the Control Reactor was 7890 mg/l. Therefore, the waste content of the Control Reactor was found to be quite different and the organic content of the first reactor was found higher than the organic contents of the other reactors.

Initial COD's were different due to the various loadings applied to each reactor. This difference in COD values was a result of the use of real landfilled solid waste instead of synthetic solid waste in the reactors. Two large volume bags were filled with solid waste at the site. The solid waste was retrieved at the site was not totally suitable for the study due to high amounts of plastic bags, household items, rocks, clothings etc. Therefore, only the pulverized part of the waste was separated and filled to the bags. Two bags were filled at the same location but from different points wherever pulverized waste was found.

Two smaller volume bags were prepared from both of the bags for every reactor. One of the small bags was discarded due to high heavy metal content and it was replaced from the other large bag. Therefore, three of the reactors were loaded from one of the bag and only one reactor was loaded from the other bag prepared at the site and this was probably the Control Reactor.

Such a result was not expected because all of the solid waste was taken from the same location. However, it appeared due to the uncontrollable nature of the landfilled solid waste.

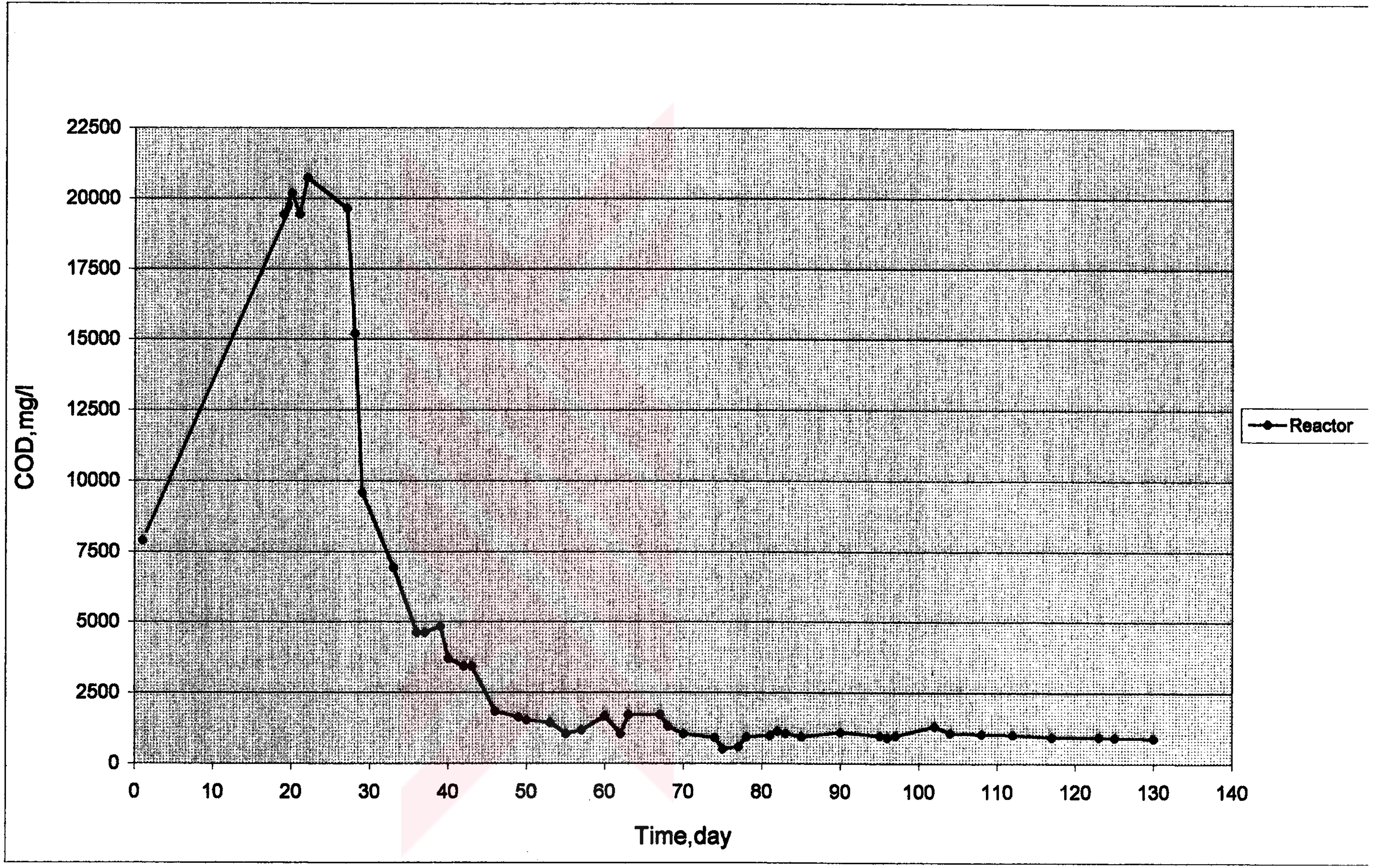

Figure 4.3. COD of the Leachate from the Reactor 1 (Control Reactor)

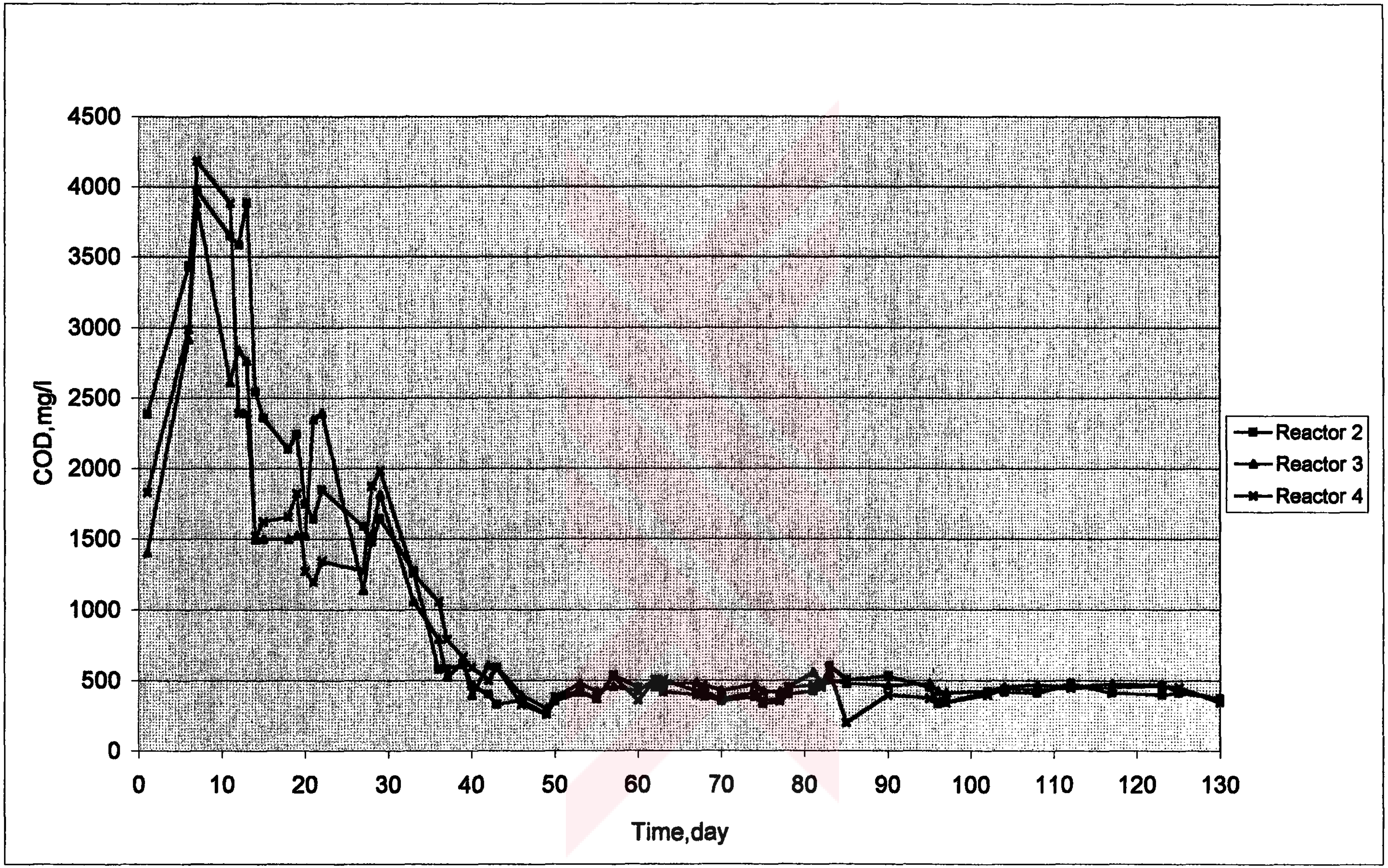

Figure 4.4. COD of the Leachate from the Reactor 2, 3, 4

The reactors with sludge addition (Reactor 2, 3 and 4) followed a similar trend in terms of COD removal throughout the study with some exceptions. An increasing trend was observed in each reactor after the first day. This was an expected trend due to the release of volatile organic acids (VOA) in the first step of anaerobic decomposition. Although this explanation could not be supported with volatile organic acid determinations in this study, this trend was observed in many other studies of anaerobic degradation. Pohland et al. stated that the majority of COD was composed of VOA during the Acid Formation Phase (1). Esteves concluded that the organic pollutant parameters like COD, BOD and TOC were following the same removal trend as the volatile acids (9). Rachdawong also found that VOA were found to be the major contributor of the COD in the initial state, since the change in COD was also reflected by a parallel change in VOAs (3).

This increase continued for a week in Reactor 2, 3 and 4. After the Day 7, COD's of these reactors began to fall gradually and this decrease continued until the Day 40 for every reactor. Some short periods when COD stayed constant were observed during this period. This decline may be attributed to the conversion of readily degradable organic materials to methane and carbon dioxide. In this period the ORP and the pH values of these three reactors which were also loaded with sludge were favorable for methanogenic activity.

The sharpest decline was observed in the Reactor 4 that was loaded with the highest sludge:waste ratio; the COD decreased to 1524 from 3885 in three days. The highest removal efficiency was also observed in this reactor in the first 25 days. When ORP data were analyzed, it was seen that the ORP values of this reactor consistently displayed the lowest values within this period. The anaerobic conversion of organic acids to methane and carbon dioxide was very efficient in Reactor 4. Therefore, it may be concluded that sludge addition was beneficial for the methanogenic activity.

After the Day 40, a significant change was not monitored in the COD values of these three reactors. The COD values stayed in the range of 260 to 400 mg/l until the last days of operation. This residual COD was because of the formation of humic acids and some other more resistant refractory organics (34).

The Control Reactor which started the anaerobic degradation with a similar trend to the other reactors, did not follow the same removal pattern. The initial increase was also monitored in this reactor. However, this increase continued for a longer time in the Control Reactor. The COD increased to 19,000 mg/l at the Day 19 and stayed at this range until the Day 27 of the experiments. A very sharp decline was observed between Day 27 and Day 36. The major anaerobic degradation of the organic content of this reactor was observed within this period. After this sharp decline, a steady decrease was observed until the Day 50 to the COD value of 1536 mg/l. A very gradual decrease was monitored then, the COD values dropped to 1000 mg/l at nearly Day 100 of the experiments. In the following days, the COD stayed constant at 900 mg/l which was the residual COD due to the presence of organics resistant to degradation.

When all reactors were compared it was seen that the reactors with sludge addition (Reactor 2, 3 and 4) followed a similar COD removal trend throughout the study with a few exceptions. This trend was quite different from the one for the Control Reactor.

First of all, the release of organic materials lasted for longer time at the Control Reactor. In a balanced system this release should be accompanied with the conversion of this released organics to methane and carbon dioxide after a short time. This prevents the organic acid accumulation in the system which may be more inhibitory for the methanogenic activity. The most important evidences of this accumulation were the ORP and pH values that were not suitable for methanogenic activity.

The anaerobic conversion started at the Control Reactor only after water addition to the system on the Day 20. This addition was probably very important for the survival of methanogens. It was also beneficial for other reactors. The water contents of the reactors were getting low for anaerobic activity; this may be concluded from the decreased amounts of gas production. Gas production increased after the moisture addition and COD removal efficiency increased in every reactor.

4.2.4 Ammonia (NH_3^--N)

Ammonia is an essential nutrient for anaerobic degradation; it is also an inhibitory by-product above certain concentrations depending upon the pH of the system. The results of ammonia measurements are presented in Figure 4.5.

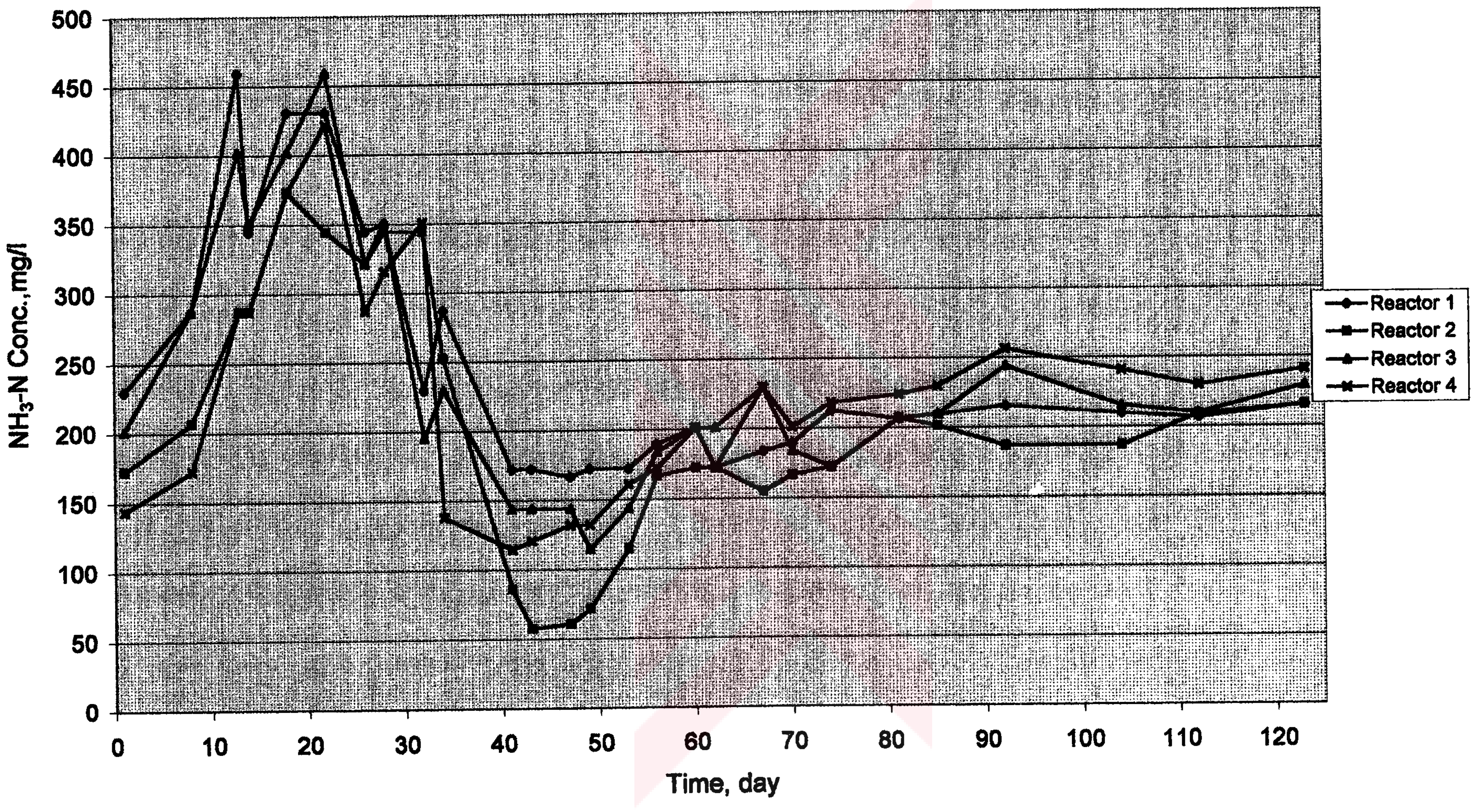

Figure 4.5. Ammonia Nitrogen of the Leachate from the Reactors

The initial ammonia values were in the range of 150-220 mg/l in the reactors. The highest observed ammonia concentration was 450 mg/l. Therefore, it may be concluded that sufficient nutrients were available throughout the study and the ammonia concentrations never reached to inhibitory levels such as 1500 mg/l in the reactors.

All four reactors displayed a similar trend in the ammonia measurements. An increase was observed first due to the release of ammonia with the anaerobic decomposition. Gallert and Winter stated that the ammonia was generated during anaerobic degradation of organic materials containing nitrogen especially urea and proteins (37).

This release of ammonia was followed by a decline in the reactors. This decline was attributed to the microbiological assimilation of ammonia that was essential for microbial activity. This bioutilization of ammonia lasted until the Day 50 and Day 60 of the study. After this period, ammonia concentrations stayed nearly constant with a small increase in the concentrations. This increase in the last portion of the experiments may be attributed to the decreasing water contents in the reactors.

Very sharp changes in ammonia concentrations were not monitored in the reactors with different sludge:waste ratios. This was also beneficial as far as the ammonia concentrations were sufficient for microbial activity. Burton et. al. expressed the drawback of enhancement activities as the generation of potentially inhibitory aqueous ammonia concentrations with the enhancement (38). However, this was not observed in the study.

4.2.5 Ortho-Phosphates

Orthophosphates were monitored as one of the major nutrients in the anaerobic degradation. The results of orthophosphates analysis are given in Figure 4.6 .

The initial orthophosphate concentrations were in 2,42 to 4,4 mg/l range in the reactors. The initially observed values in the reactors with sludge addition were close to each other and higher than the concentration of the Control Reactor. This may be attributed to the supply of nutrients to the systems by anaerobically digested sludge addition.

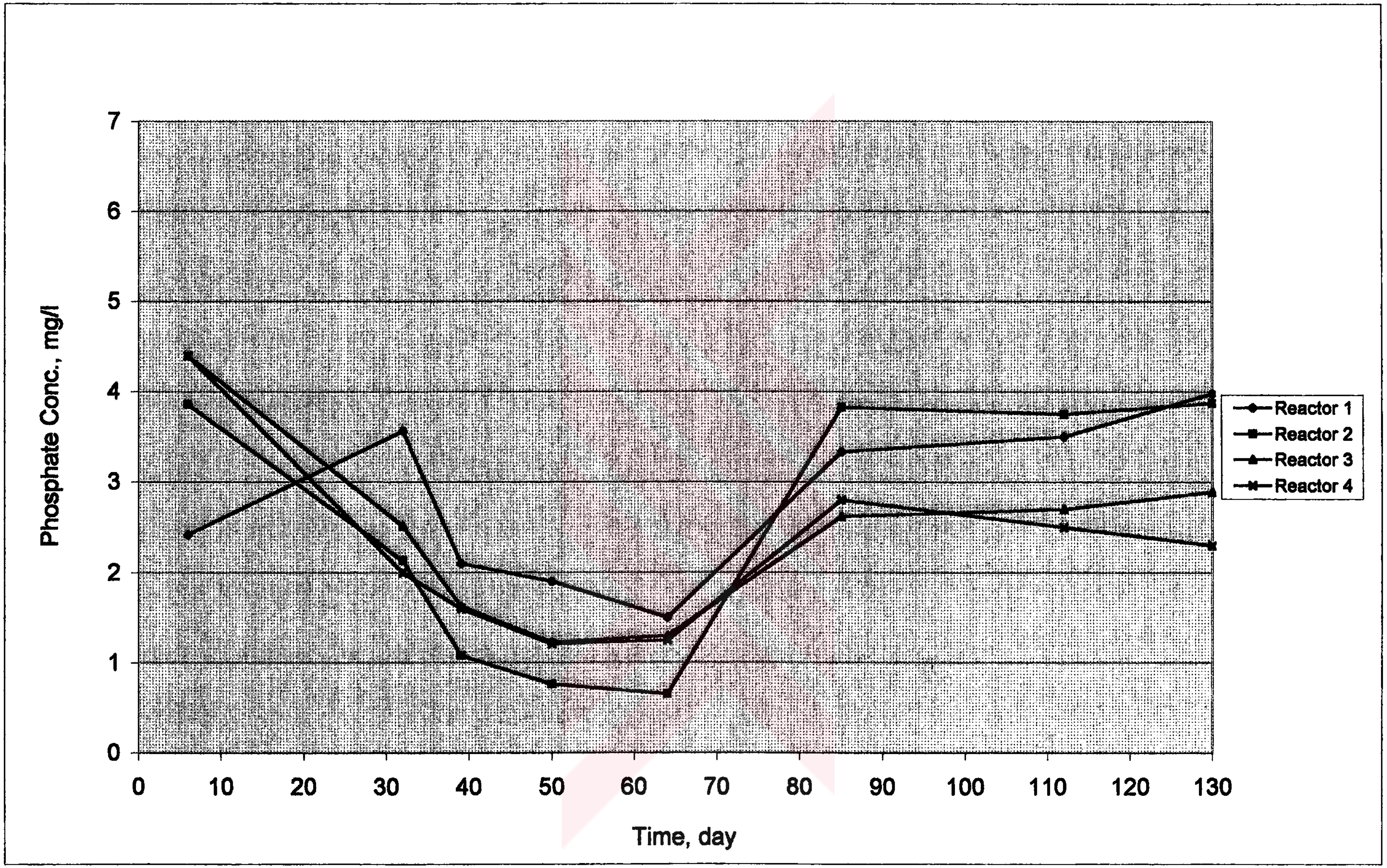

Figure 4.6. Orthophosphate of the Leachate from the Reactors

Very sharp declines were observed in the Reactors 2, 3 and 4 after the first analysis day and this decline lasted for 50 days and then stayed constant for 15 days. This decline was consistent with the active anaerobic degradation phase in which high COD removals were observed. Therefore, the decline was attributed to the biological assimilation of orthophosphates during the anaerobic degradation.

A similar decline was not observed in the Control Reactor. The orthophosphate concentrations stayed approximately constant for a period and then a declining trend started at in this reactor, this was also consistent with the later anaerobic degradation phase observed in this reactor.

After the 40th day, the reactors followed a similar trend. The orthophosphate concentrations were constant for 15 days in the reactor and then showed a gradual increase that was followed by a constant concentration period. This period lasted until the end of the study. The period in which the phosphate concentration stayed constant as expected after the active methanogenic phase. However, the increase that followed this period was not related to the microbiological activities. This might be due to evaporation effects; the decrease in the water level of the reactors.

It may also be concluded that the orthophosphate concentrations in the reactors were sufficient for anaerobic degradation throughout the study.

4.2.6 Alkalinity

The alkalinity and the volatile organic acids comprise a significant portion of the acidic and basic constituents which may accumulate during anaerobic degradation (39). It is also evident that acid base equilibrium is responsible for maintaining a buffered environment for the degradation. The alkalinity was monitored approximately once a month and the results of these analyses were given in Figure 4.7.

The first alkalinity measurements were performed on the Day 20 of the experiments. The initial alkalinity values of the reactors with sludge addition were approximately 1500 mg/l as $CaCO_3$ but the alkalinity of the Control Reactor (Reactor 1) was quite low when compared to the other reactors. When the pH and the COD data of the same period were

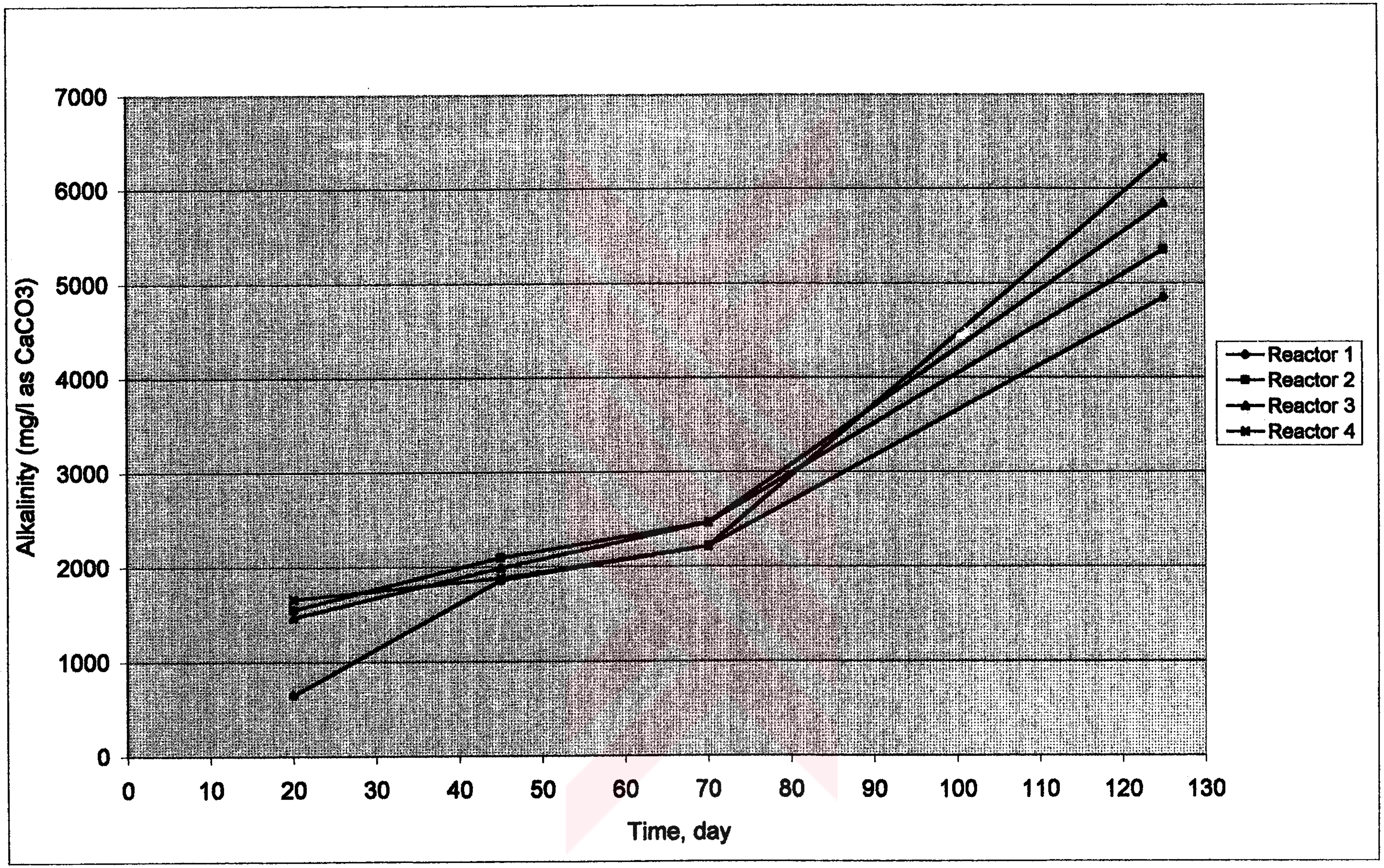

Figure 4.7. Alkalinity of the Leachate from the Reactors

analyzed, it was seen that the Control Reactor was displaying low pH values and high constant COD values. This was attributed to the accumulation of organic acids in this period. The alkalinity was not high enough to neutralize these acids and therefore pH decreased.

However the alkalinity of the Reactor 2, 3 and 4 were high and displayed a smooth slightly increasing trend until the Day 75. This was due to the decrease in the volatile acid concentrations of the reactors as it was concluded from the COD removal data. The alkalinity of the Control Reactor reached to the concentrations of the other reactors and then the alkalinity showed increased in all four reactors. This increase is due to the decrease in the organic acid concentrations at the last days of the decomposition and also due to evaporation of water in the reactors.

The alkalinities of the reactors with sludge addition were high enough to buffer the systems throughout the study as understood from the pH and COD data. The pHs of the reactors were always in 7.0-8,5 range and no souring occurred in the reactors. This problem was observed in the Control Reactor. Therefore, it may be concluded that anaerobically digested sludge addition was beneficial for maintaining a buffered environment during the anaerobic degradation.

4.2.7 Chloride

Chloride (Cl^-) was used as a non-reactive, tracer component to estimate the dilution and evaporation effects in this study. Chloride monitoring started on the Day 57 of the study and the results of this monitoring is displayed in Figure 4.8.

Chlorine removal by sorption and exchange reactions is quite insignificant. It is not also affected by the biological mechanisms and due to its high solubility, chemical precipitation is not and active removal mechanism for chloride (9). Therefore, the changes in the chloride concentration may show the dilution caused by water additions, evaporation and sampling.

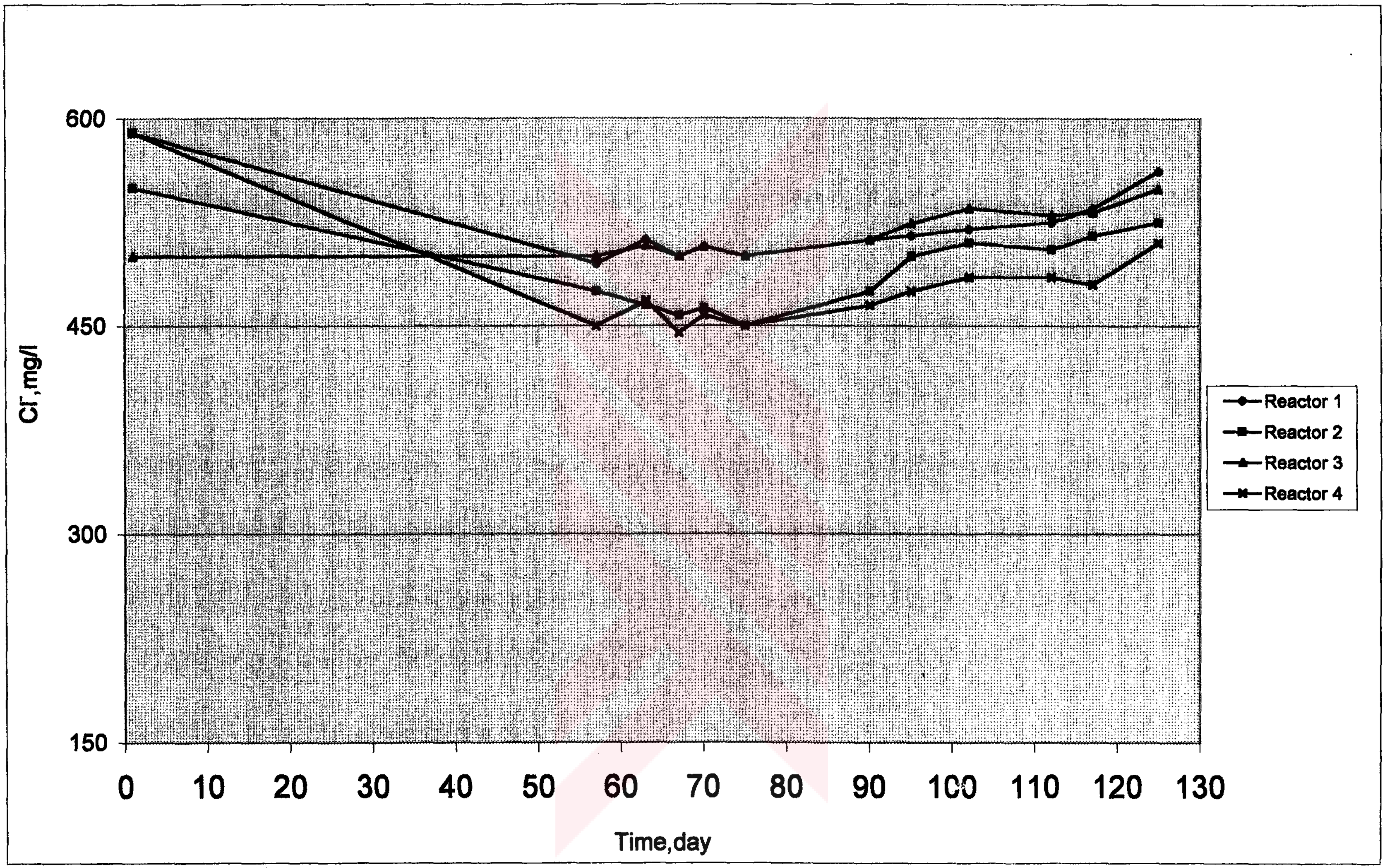

Figure 4.8. Chloride of the Leachate from the Reactors

The effects of dilution and evaporation in the first weeks could not the observed because the chloride measurements started on Day 57. Therefore, the effects of water addition on the Day 20 of the experiments could not be seen form the chloride concentration pattern.

Initial chloride measurements showed that chloride concentrations stayed more or less constant up to Day 75. The next measurement was done on the Day 90 and increased chloride concentrations were observed on that day. Then the concentrations stayed constant for a period and displayed an increasing trend afterwards.

The increasing trends observed in the chloride concentrations were attributed to the evaporation of the water in the reactors. This was also consistent with the increases observed in the concentrations of the other parameters such as ammonia, alkalinity and phosphate after the Day 60 and Day 70. It was due to the fact that although water was lost by sampling and especially evaporation, any water addition was not performed throughout the study except the Day 20.

4.3 Analysis of the Gas Production and Gas Composition

The results of gas production analysis are given in Figure 4.9 and 4.10 as the daily gas production and the cumulative gas production, respectively and the Figure 4.11, 4.12, 4.13, 4.14 give the results of gas composition analysis.

4.3.1 Analysis of Gas Production

4.3.1.1 Daily Gas Production

Daily gas production was estimated by recording the observed amount of gas produced in 24 hours. Whenever gas readings were not taken on two consecutive days, daily gas productions were not taken into consideration. The daily gas productions of the reactors are presented in Figure 4.9.

The capacities of gas collection units play an important role in the readings of the daily gas productions. If the capacity of the gas collection unit was exceeded 24 hours after the last

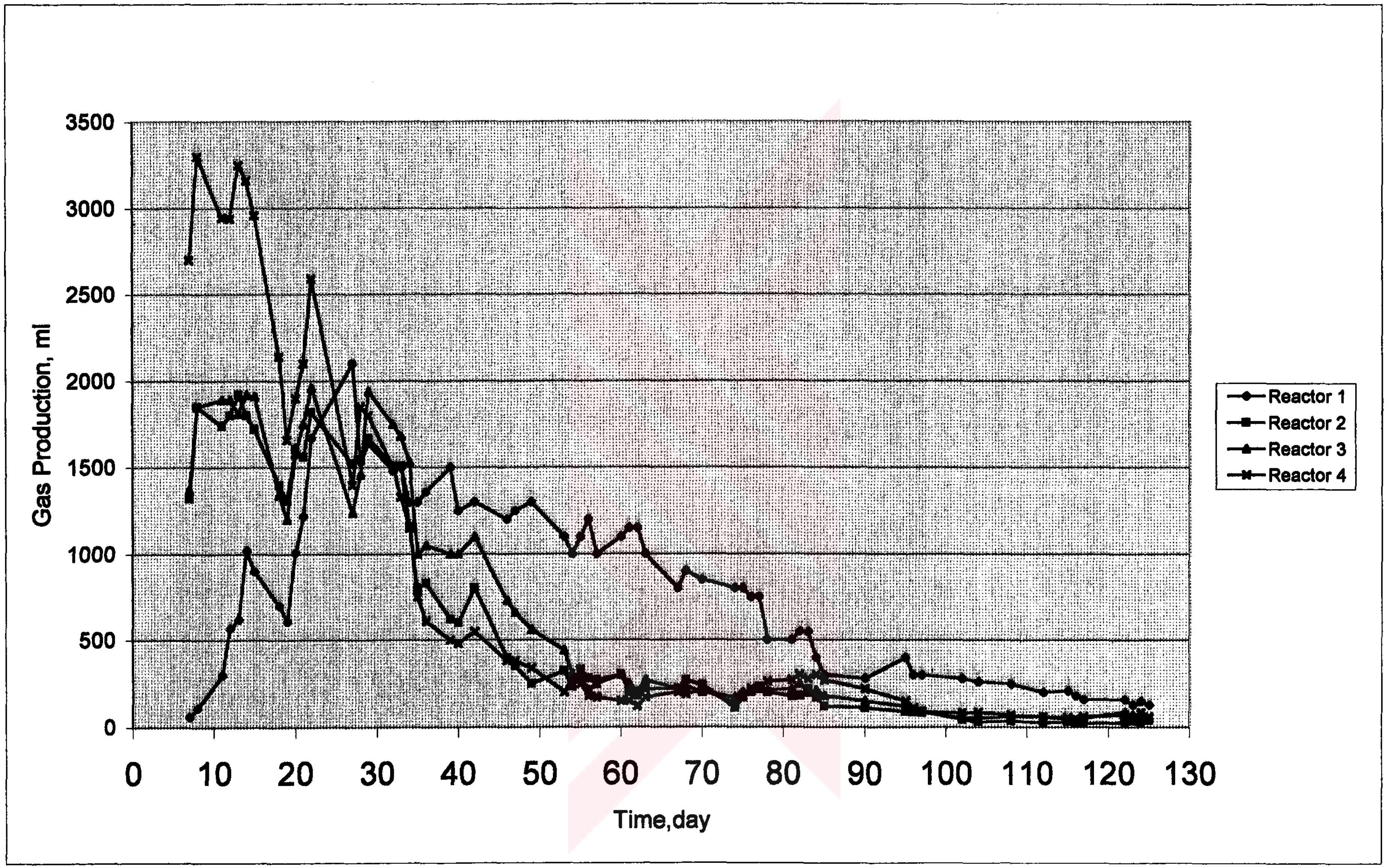

Figure 4.9. Daily Gas Production of the Reactors

reading, the actual gas production could not be determined and the capacity of the unit was taken as the daily production. Therefore the actual gas productions may be higher than the recorded values.

The initial gas production rates were quite different in the reactors. High gas production rates were observed in the reactors with sludge addition as soon as the reactors were loaded. However, the Control Reactor displayed a gradual increase beginning from the first day.

In the first 15 days, the daily gas production of the Reactor 4 was in 2700-3300 ml range. Reactor 2 and 3 were in 1330-1900 ml range in this period and these two reactors showed nearly the same gas production trend in these days. The daily gas production of the Control Reactor did not exceed 0-1020 ml range in the start-up period.

It was observed that the initial daily gas production was much higher at the Reactor 4 that was loaded with the highest sludge addition. This production decreased in the reactors with the decreasing amount of sludge addition and the lowest gas production was observed at the Control Reactor. Therefore high gas production rate may be attributed to the anaerobic degradation enhanced with sludge addition. The highest COD removal in the reactors was also observed in this period of highest gas production.

A sharp decline began at the Day 13 and 14 in each reactor. This was attributed to the decreased water level at the reactors due to evaporation. Therefore, 250 ml of water was added to the reactors on the Day 20. After this addition, gas productions increased in the reactors again. This proved that the decline in the gas productions was due to decrease in the moisture content. The gas production showed small fluctuations in the following day 10-15 days. This period was also the only period when the daily gas production of all reactors was at the same level, in the 1500-2000 ml range.

After this period where gas productions were in the same levels, the reactors with sludge addition and the Control Reactor displayed different patterns. The reactors with sludge addition showed a sharp decline until the Day 50 and the gas production stayed approximately constant between Day 50 and Day 90; then decreased to nearly zero gas production gradually until the last day of the analysis. This period of low gas production was consistent with the period that COD values of the reactors were constant. These observations showed that the stabilization of the waste was nearly complete in the three reactors reflected with the decrease in the gas production.

However, the decline of daily gas production in the Control Reactor was not as sharp as the ones at the other reactors. Control Reactor that showed its peak gas production rate as 2100 ml., on the Day 27, the daily gas production decreased gradually to 750-500 ml range from the 1500-2000 ml range.

It was due to the fact that stabilization was going on in this reactor and therefore the gas production rate did not decreased like the other reactors that completed stabilization earlier. A very gradual decline to zero production was recorded at the Control Reactor until the last day.

When daily gas productions of the reactors were compared, it was seen that the period of gas production was shortest at the Reactor 4 with the highest sludge addition, this period got longer with the lower sludge additions. As an example, the daily gas production was recorded below 200 ml after the Day 53 in the Reactor 4, this period extended to 113 in the Control Reactor. The stabilization period was much longer in the Control Reactor. Therefore, it may be concluded that the sludge addition was enhancing decomposition and keeping the favorable gas production in a shorter duration.

4.3.1.2 Cumulative Gas Production

Cumulative gas production was calculated by summing all of the observed daily gas production within the experimental period. Therefore the cumulative gas production changed according to daily gas production data. The total gas productions of the reactors are given in Table 4.3;

Table 4.3 Total Gas Production of the Reactors

Reactor	Total Gas Production (l)	Time Required to Reach Max. Production
Reactor 1	51	95
Reactor 2	40	65
Reactor 3	44	60
Reactor 4	51.5	53

The cumulative gas productions of the reactors are presented in Figure 4.10. A sudden increase was observed in the reactors with sludge addition in the first days. As expected, this increase got smoother at every reactor after a certain period. The reactors that completed stabilization reached this state earlier due to decreasing amounts of gas production.

Until the Day 57, the order of the volume of cumulative gas production was parallel to the amount of sludge addition. However, Control Reactor which has the lowest cumulative gas production curve reached the same volume of gas production with Reactor 2 on this day and the 10% sludge added reactor (Reactor2) was the one with the lowest cumulative gas production after this day. The Control Reactor also reached to the 14% sludge added reactor (Reactor 3) within a ten days time. It could catch the 20% sludge added reactor (Reactor 4) at the last days of the experiment.

Before comparing these results, the relatively high initial COD of the Control Reactor should be taken into consideration. This high value indicated that the organic content of this reactor was much higher than the other ones. Therefore a higher gas production was expected in this reactor. As a result, it might be wrong to compare the cumulative gas productions of the reactors with the Control Reactor due to different organic content.

If the reactors with sludge addition were compared to each other, it was seen that the reactor with the highest sludge addition gave the highest cumulative gas production; these productions decreased with the decreasing sludge:waste ratio of the reactors. It was also

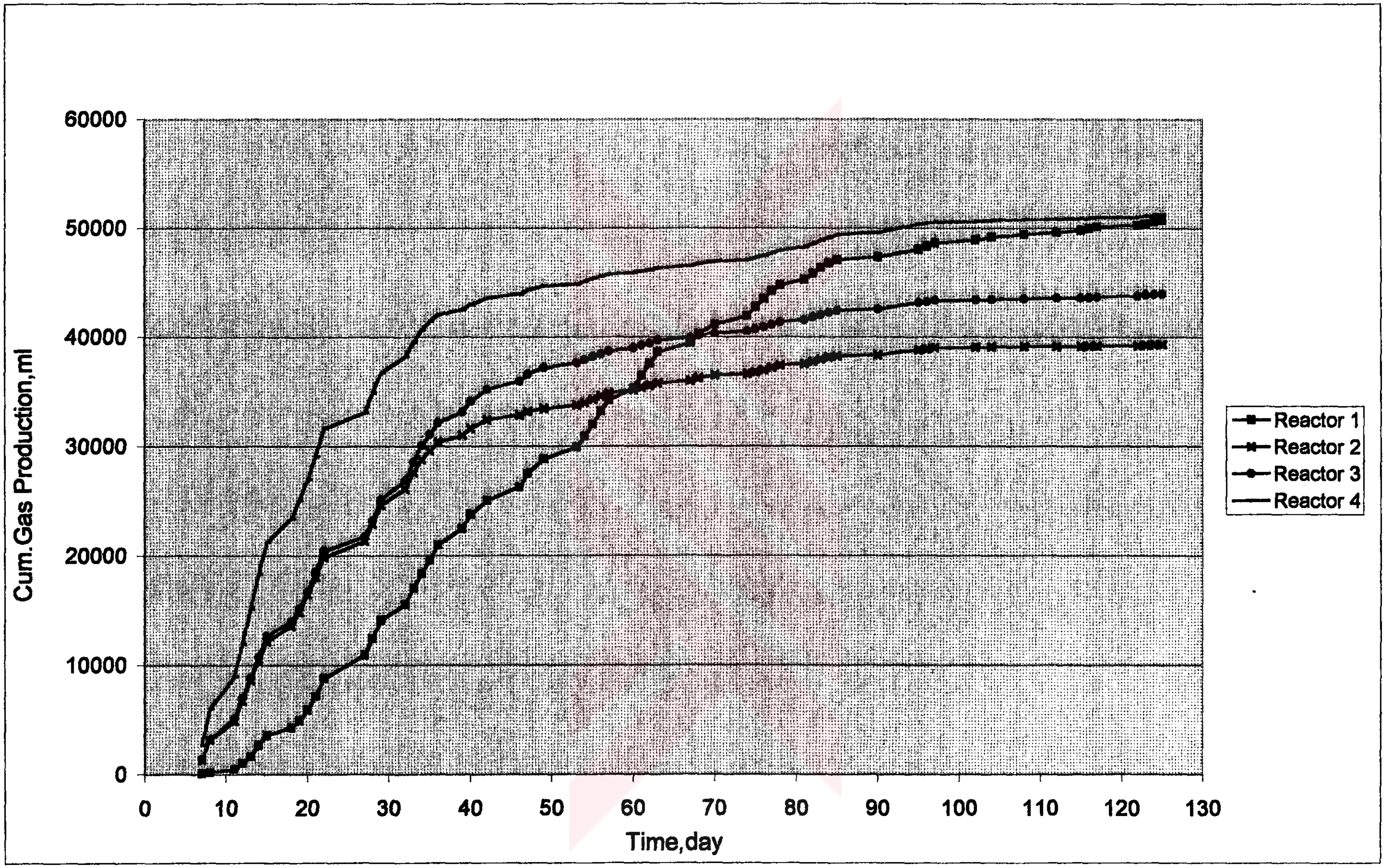

Figure 4.10. Cumulative Gas Production of the Reactors

observed that the time required for stabilization was getting shorter with the higher sludge addition.

The sharpest declines in the COD values were also observed in the reactor that was loaded with the highest sludge addition. These declines and also the high gas production reflected that the removal efficiency was high in this reactor.

4.3.2 Analysis of the Gas Composition

Gas composition analysis started at the Day 33 of the study. The gas composition results of the reactors are given in Figures 4.11, 4.12, 4.13, 4.14.

Although the first 30 days could not be monitored, the first gas composition readings showed the degree of stabilization reached within this period. The methane percentage in Methane Formation Phase was given in 30 to 60 percent (29). It was seen from the first readings that methane concentrations were within this range in every reactor and therefore it might be concluded that all reactors were in the methane formation phase. It was due to the fact that the solid waste was partially stabilized when it was retrieved. This was also obvious from COD and ORP data.

The first 30 days that could not be monitored was an important period because the stabilization started very early especially in reactors with sludge addition and therefore the transition from aerobic to anaerobic conditions and acid formation phases could not be detected in the gas composition analysis.

When gas composition data of the Control Reactor were analyzed, it was observed that methane (CH_4) percentage in the generated gas was within the 30-46 % except one point, which was 25 %. These high percentages were due to the fact that the transition to methane formation step from acid formation step had taken place later in this reactor because of the souring problem faced. Therefore, the methanogenic phase was monitored from an earlier point in this reactor and as a result the methane percentages were high during the monitoring period. Some fluctuations in the readings were attributed to loss of sample during the transport; as an example, 64% air was measured on the Day 63, this may be due to a leakage in the sampling tubes. The methane percentage began to decrease as expected

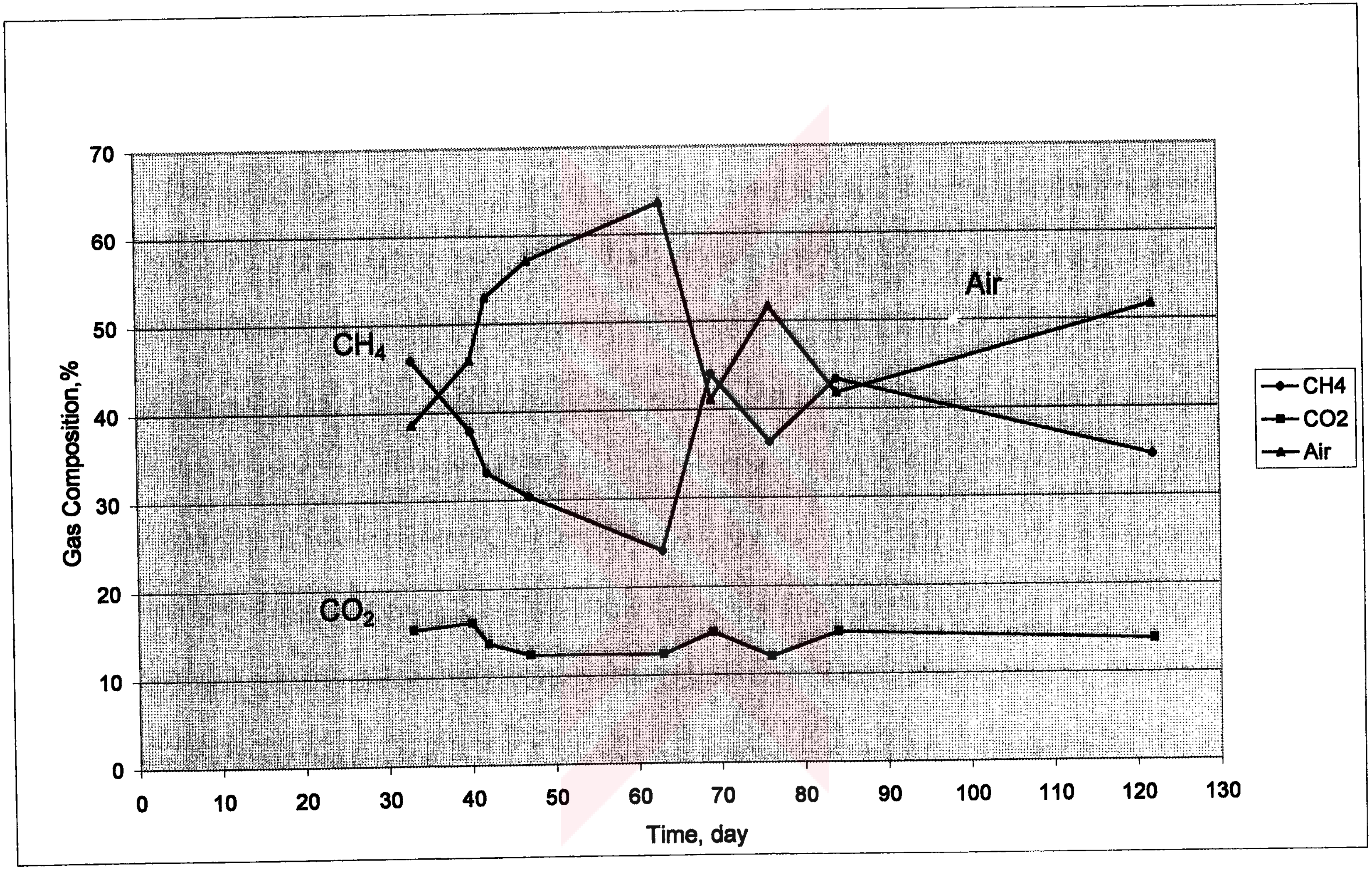

Figure 4.11. Gas Composition of the Reactor 1

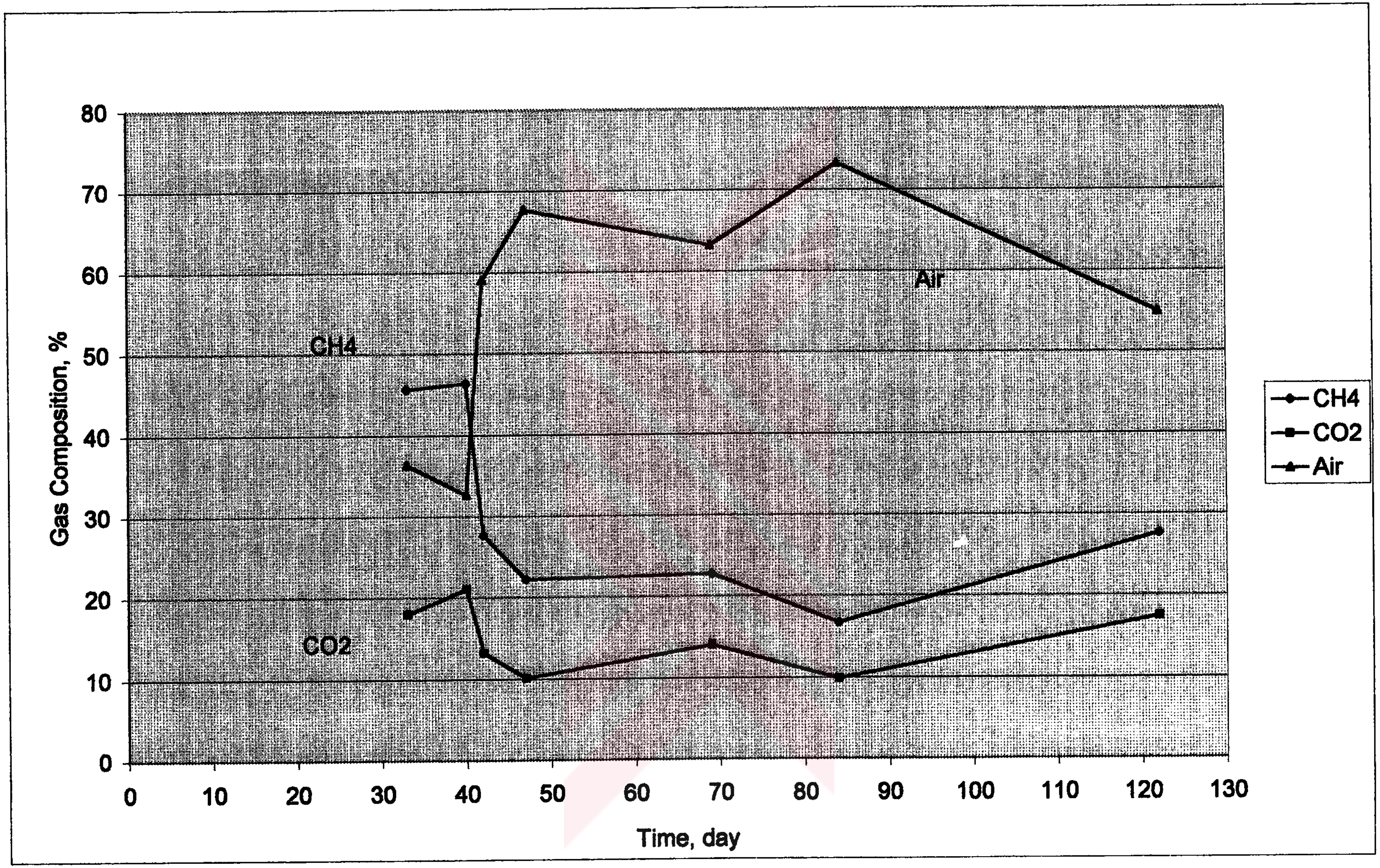

Figure 4.12. Gas Composition of the Reactor 2

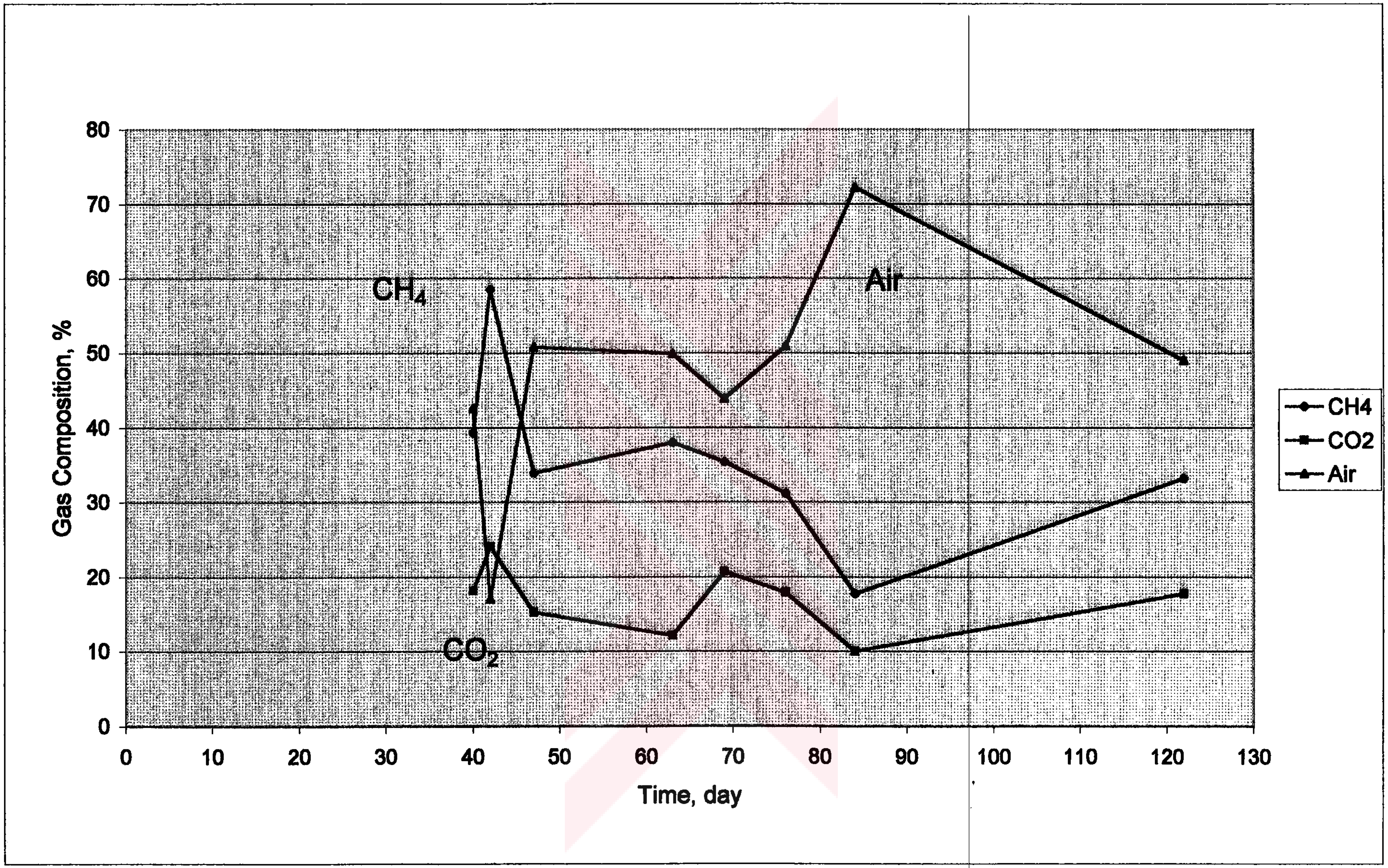

Figure 4.13. Gas Composition of the Reactor 3

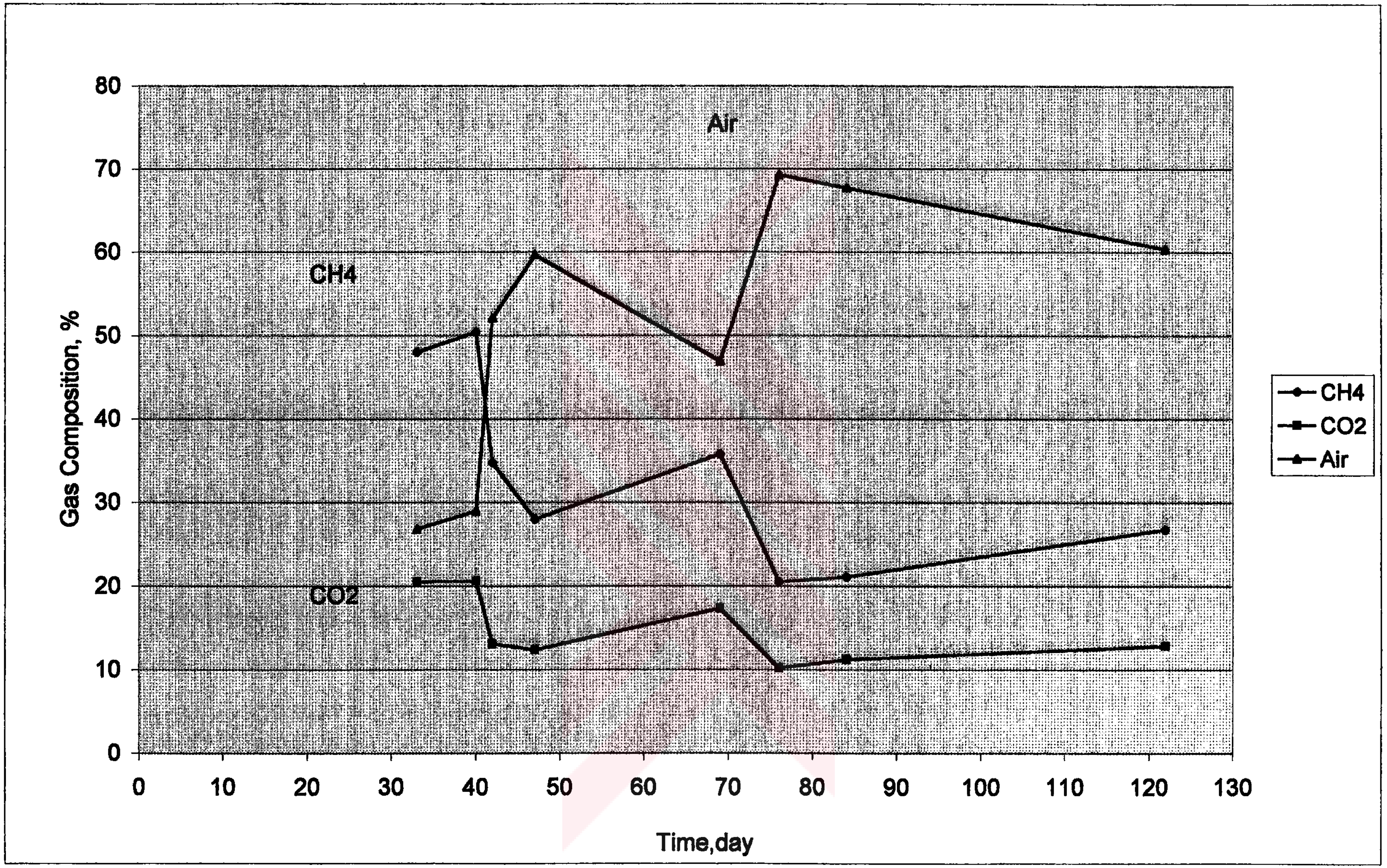

Figure 4.15. Gas Composition of the Reactor 4

through the last days of the study. The carbon dioxide (CO_2) percentage stayed nearly constant at 12-16 % range throughout the study.

The Reactor 2 was the reactor that gave the lowest methane yield among all reactors. The methane percentages were above 40% only in the first 42 days. Then methane concentrations were observed within 17-27 %. A decrease was expected in this period due to the limitations in organic materials. However, the methane concentrations did not fall to these ranges in any of the reactors. The air concentration on four of the analysis days were above 70%, two of these points were not plotted to the graphs because the air concentration was above 95 % in these points. Therefore, the low methane yield observed in this reactor might be due to incorrect data obtained from unproperly sealed samples. This might also be due to an inhibitory substance for methane generation in the system. The carbon dioxide (CO_2) was within 10-20 % range in this reactor throughout the study.

Reactor 3 displayed quite high methane percentages during the study; methane did not fall below 30 % except one point and the highest methane was detected on the Day 42 with a 59 %. A decline to 35% was detected at the following reading and the methane percentage stayed approximately constant after that. Reactor 3 was also in Methane Formation Phase as understood from gas composition data.

In Reactor 4 which was loaded with the highest amount of sludge, 50% methane concentrations were detected in the first two readings, on the Day 33 and 40, respectively. However, a decline to 30-35 % was observed after these readings. A second decline was also observed to 20 %. This was an expected trend as understood from the COD removal data; this reactor entered methane formation phase earlier than the other reactors. Therefore, it was expected to complete this step earlier. As a result, a decline in the methane concentrations was observed.

All four reactors were found to be in the methane formation stage as understood from the gas composition data. The first readings were above 40 % for each reactor, in a range that was typical for methane formation phase. In the following readings, the methane concentrations of the reactors loaded with sludge were found lower than the concentrations of the Control Unit. It was due to the fact that this reactor had started anaerobic degradation later than the other reactors and therefore the methanoganic stage was monitored from an earlier stage. The other reactors that entered this stage earlier as understood from the COD removal trend, displayed a decline in methane concentrations as expected in the later steps of methanogenic phase. This decline was because of substrate limitations and gradual reversion to aerobic stage.

4.3.3 Cumulative Methane (CH_4) Production

Cumulative methane productions were obtained by using daily gas production and gas composition data together. The methane percentage was multiplied by the daily gas production of the analysis day to determine the volume of methane production on that day. This estimation was performed for every day of gas composition analysis. The methane production of days in between two consecutive gas composition analyses was obtained by multiplying the daily gas volume by the average of the methane readings of the two consecutive days. The cumulative methane production was displayed in Figure 4.15

The gas composition analysis started on the Day 33 of the study. Therefore, in order to determine the cumulative methane production of the first 30 days, an assumed gas percentage was necessary. This 30 days was the period in which the highest gas production was observed in Reactors 2, 3, 4; this period was also the one with the highest methane percentage of these reactors because it was the active methanogenic phase as it was concluded from the COD and gas production data. The same estimation method of cumulative methane production was also used for this period; the methane percentage obtained on the first analysis day (Day 33) was used for the period before this date.

The total volume of methane production in Reactor 1, 2, 3 and 4 are 19.1 lt, 15.9 lt, 17.8lt and 22.8 lt., respectively. The comparison of the Control Reactor with other reactor may be misleading due to the same reasons expressed in gas production section because gas production affected the cumulative methane analysis directly.

Therefore, a comparison between the reactors with sludge addition would be preferred to a comparison with the Control Unit. If Reactors 2, 3 and 4 were compared, it was seen that the higher sludge:waste ratio gave the highest methane yield.

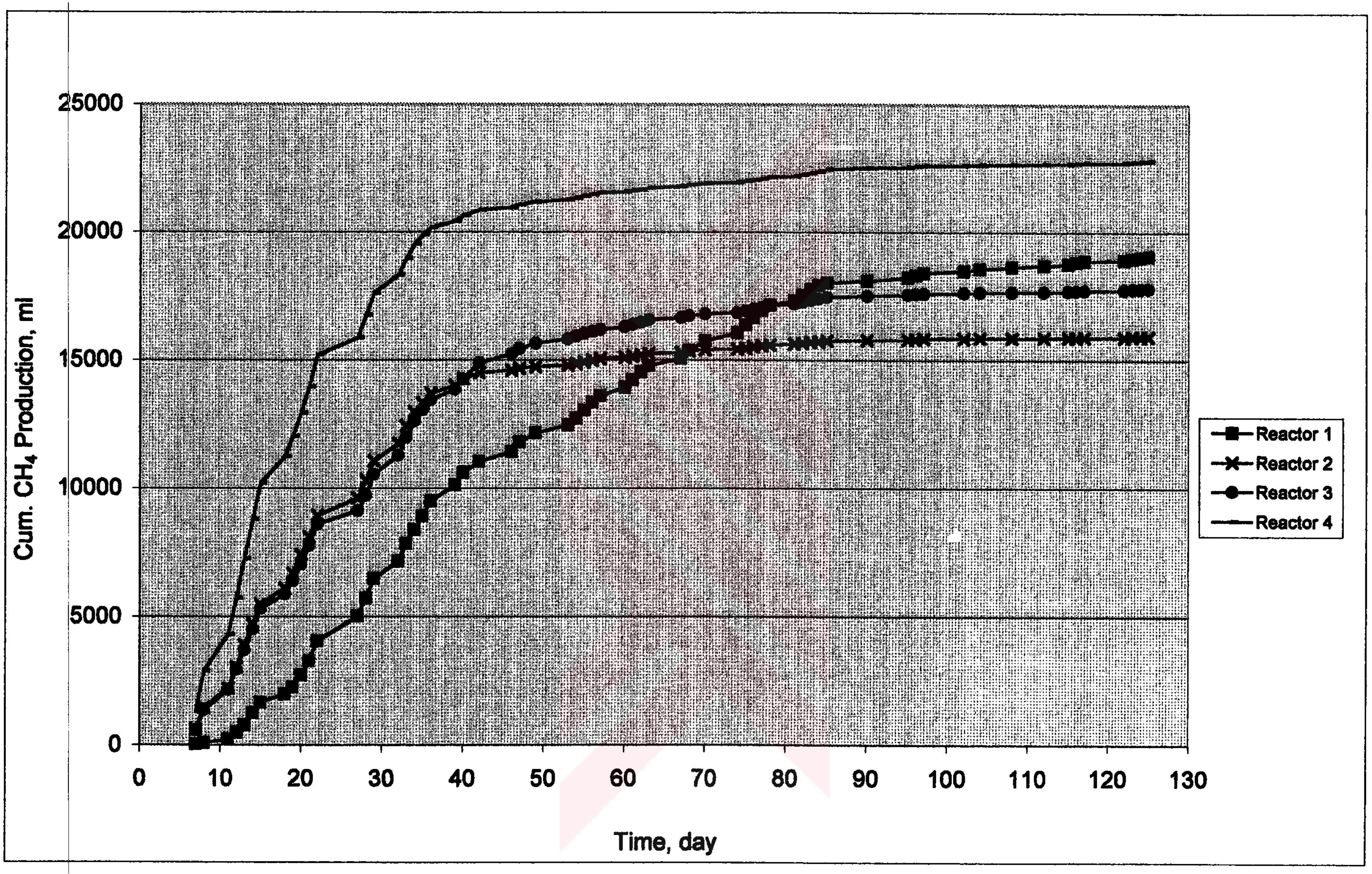

Figure 4.15. Cumulative Methane Production of the Reactors

Therefore, it may be concluded that sludge addition was beneficial for obtaining higher methane production. The optimum sludge:waste ratio for the highest methane production was 1:4 ratio which was the highest ratio used in the study.

5. SUMMARY AND CONCLUSIONS

In this study, the remaining stabilization potential of solid waste retrieved from an operating landfill was investigated by the anaerobic digestion of the waste with the addition of anaerobically digested sludge. For this purpose, four reactors were placed in a temperature controlled aquarium and loaded with different sludge to waste ratios in order to determine the remaining stabilization potential, by means of the optimum sludge:waste ratio for the highest methane yield. Furthermore, the use of sludge as an enhancement technique for the waste degradation and also an alternative sludge disposal option were evaluated. According to these objectives, the specific results can be given as follows;

1. In order to reach the objectives, the following experiments were performed throughout the study. Leachate samples were analyzed for pH, ORP, COD, orthophosphate, ammonia nitrogen, chlorine and alkalinity; and in the gas generated, the volume of daily gas production and the gas composition were the monitored parameters. The experimental results are as follows;

   The pH values of all reactors exhibited a similar trend throughout the study. The pH of the reactors stayed in the 7-8.5 range throughout the study except the decline observed at Control Reactor until 5.78 in the first 30 days. This deviation was attributed to a possible souring problem observed in this reactor which could be explained as the production of the organic acids more rapidly than they are converted to methane and carbon dioxide and this inhibited the methanogens. The water addition performed on the Day 20 of the study caused dilution in the reactor and solved the souring problem. Except this deviation, it was observed that pH values was always in the range that methanogens can proceed and also they were close to the optimum range for methanogenic activity given as 7 to 7.2 (2). The souring problem was not observed at the reactors with sludge addition indicating that addition of sludge was beneficial for the establishment of the suitable conditions for the methanogens.

The initial ORP values were negative and very sharp declines (especially in the reactors with sludge addition) were observed after these initial values indicating the establishment of highly reducing environments. The period that the ORP values showed a sharp decline was also the one where an extensive COD removal took place in the reactors. This supports the fact that highly reducing condition is a prerequisite for the efficiency of methanogenic activity (3). After the Day 80, the ORP values started to increase to initial values in every reactor. This was also the period when COD removal and gas production were quite low. Therefore it may be concluded that the stabilization was about to be completed and the oxidizing conditions were beginning to reestablish in the reactors. Every reactor displayed the same trend in the ORP values, however it was observed that the reducing conditions and also the oxidizing conditions at the end of the study were monitored earlier at the reactors with the high sludge addition which could be attributed to the enhancement of degradation with the sludge addition.

When all reactors were compared, it was seen that the reactors with sludge addition (Reactor 2, 3 and 4) followed a similar COD removal trend throughout the study with a few exceptions. A release of organic content was observed as understood from the increasing COD values, then this increase was followed with a decreasing trend with the conversion of volatile organic acids to methane and carbon dioxide. This conversion was followed with period of steady conditions where residual COD was seen. This residual COD was because of humic acids and more residual organic content (34). Although the same release and conversion periods were observed in the Control Reactor, the release of the organic content lasted for a much longer time. It was not only due to the higher organic content of solid waste loaded to the reactor and but also due to the souring problem observed in this reactor; it is because a very sharp decline was observed in the COD values after the water addition that caused dilution in the reactor. The pH and the ORP data also supported that the conditions became suitable for the methanogens after this water addition performed on the Day 20.

Ammonia and ortho-phosphates were the two essential nutrients monitored in the study. It was seen that both nutrients were sufficient for anaerobic degradation throughout the study and ammonia concentrations never reached to the inhibitory levels such as 1500 mg/l in the reactors.

All four reactors displayed the same removal trend in the ammonia measurements. An increase was observed due to the release of ammonia and this increase was continued with a decline attributed to the microbiological assimilation of the nutrient. An increasing trend was observed at the last days, this increase was due to the evaporation effects in the reactors.

In the orthophosphate measurements, very sharp declines were monitored at the beginning that lasted for 50 days. This decline was consistent with the active anaerobic degradation period and attributed to the biological assimilation of the nutrient. The orthophosphate concentrations stayed constant for a period and then a gradual increase was observed. This was also due to the evaporation effects observed in the reactor.

Alkalinity was another parameter monitored in the leachate samples. An increasing trend was observed in the alkalinities of the four reactors. This was due to the decrease in the volatile acid concentrations in the reactors as it was also supported from the COD removal data and also due to evaporation of water in the reactors in the last days of the study. Only difference between the Control Reactor and the other reactors was in the initial alkalinity values, the alkalinity of the Control Reactor (Reactor 1) was quite low when compared to the others.

Chloride was monitored as a tracer to estimate the dilution and evaporation effects. The chlorine concentrations stayed constant for 75 days and started to increase after this measurement that was attributed to the evaporation of the water in the reactors. This also supported that the increase observed in the concentrations of the other parameters in the last periods were due to the evaporation effects.

When daily gas productions of the reactors were compared, it was seen that the period of gas production was shortest at the Reactor 4 with the highest sludge addition, this period got longer with the lower sludge additions.

The total gas production in the reactors were recorded as follows; Reactor 1 (Control Reactor) 51 l; Reactor 2, 40 l; Reactor 3, 44 l and Reactor 4, 51.5 l. Before comparing these results, the relatively high initial COD of the Control Reactor should be taken into consideration, a higher gas production was expected in this reactor. As a result, it might be wrong to compare the cumulative gas productions of the reactors with the Control Reactor due to different organic content.

If the reactors with sludge addition were compared to each other, it was seen that the reactor with the highest sludge addition gave the highest cumulative gas production; this production decreased with the decreasing sludge:waste ratio of the reactors.

Gas composition was also monitored in the generated gas. The gas composition data showed that all four reactors were found to be in the methane formation stage because the first readings were above 40% for every reactor, in a range that was typical for methane formation phase. In the following readings, the methane concentrations of the reactors loaded with sludge were found lower than the concentrations of the Control Unit. It was due to the fact that this reactor had started anaerobic degradation later than the other reactors and therefore the methanoganic stage was monitored from an earlier stage. The other reactors that entered this stage earlier as understood from the COD removal trend, displayed a decline in methane concentration as expected in the later steps of methanogenic phase. This decline was because of substrate limitations and gradual reversion to aerobic stage.

2. Addition of anaerobically digested sludge was found beneficial for the rate and the extent of stabilization of solid waste.

    a. Anaerobically digested sludge addition was beneficial for the establishment of anaerobic conditions at the start-up period. When the pH and the ORP data were analyzed, it was seen that the conditions were suitable for the survival of methanogens from the beginning of the study.

       The initial pH values of these reactors were in a range that methanogens were active (7.5 to 8) and the initial ORP values were observed to be decreasing with the sludge:waste ratios at the reactors with the highest ORP at Control Reactor. Therefore it may be concluded that the addition of anaerobically digested sludge was beneficial for the establishment of reducing conditions at the start-up period.

The most important problem encountered in the Control Reactor was a souring problem at the start-up period. However, this souring problem was not monitored in the reactors with sludge addition. As Barlaz stated, the methanogens control the pH of their ecosystem by the consumption of the acetate (26). When the activity of the fermentative organisms exceed that of the methanogens, there will be an imbalance in the system, acids and hydrogen accumulate, the pH drops and methanogens are inhibited (26). Souring was not observed in the reactors with sludge addition because sludge served as a seed of active methanogens as well as necessary nutrients. It should also be added that the sludge used was a neutral sludge that might also be helpful against souring.

The long start-up period in the Control Reactor could not be attributed to the higher organic content of the Reactor because the COD values dropped drastically when the souring problem is overcome with water addition to the system. As the moisture content of the system was increased, dilution was achieved, the opportunity of the contact of the microorganisms and the substrate increased.

b. With an efficient start-up, the reactors with sludge addition that started anaerobic stabilization earlier, completed stabilization in a shorter time when compared to the Control Reactor. It was due to the following facts; the sludge addition supplied an active biomass to the reactors as understood from the COD removal trends, the sludge addition also supplied nutrients to the system such as phosphate as concluded from the results of the initial phosphate measurements, this addition also supplied buffer to the systems as understood from the initial alkalinity results and therefore an initial pH decrease was eliminated.

Therefore, the sludge addition caused enhancement of stabilization in the reactors and these reactors completed active degradation earlier than the Control Reactor. This conclusion was also supported by the gas measurements; when daily gas productions of the reactors were compared, it was seen that the period of gas production was shortest at the Reactor 4 with the highest sludge addition, this period got longer with the lower sludge additions.

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When the total gas production was estimated, the reactors gave the following results; Reactor 1 (Control Reactor) 51 l; Reactor 2, 40 l; Reactor 3, 44 l and Reactor 4, 51.5 l. If the reactors with sludge addition were compared to each other, it might be concluded that the reactor with the highest sludge addition gave the highest cumulative gas production; these productions decreased with the decreasing sludge:waste ratio of the reactors.

A comparison between the Control Reactor and the other reactors was not done due to the relatively high initial COD of the Control Reactor indicating a higher organic content of the reactor. As a result, it might be wrong to compare the cumulative gas productions of the reactors with the Control Reactor due to different organic content.

Cumulative methane production was another estimated parameter. The total volume of methane production in Reactor 1, 2, 3 and 4 are 19.1 lt, 15.9 lt, 17.8 lt and 22.8 lt., respectively. If only the reactors 2, 3 and 4 were compared due to the same reasons expressed above, it was observed that the higher sludge:waste ratio gave the higher methane yield. It is due to the fact that the gas production and the methane percentages were getting higher with the higher sludge:waste ratios.

As a conclusion, the reactor with the highest sludge:waste ratio as 1:4 was the reactor where the most enhanced and efficient degradation was observed. It should also be added that this ratio was the highest possible ratio due to the operational difficulties. Therefore, the investigation of any higher ratios was not reasonable even it might result in higher methane yield.

4. One of the objectives of the study was to find the sludge:waste ratio for the optimization of the methane recovery. It was seen that the reactor with the highest sludge addition gave the highest methane yield among the reactors loaded with sludge. Therefore, it may be concluded that sludge addition was beneficial for obtaining higher methane production. The optimum sludge: waste ratio for the highest methane production was 4:1 ratio which was the highest ratio used in the study. Changes in some of the selected parameters during stabilization in Reactor 4 are presented in Figure 5.1 and 5.2.

5. Due to the beneficial effects of sludge addition on waste stabilization, the codisposal of anaerobically digested sludge with solid waste was found as a possible disposal option of the sludge. For this disposal, 1:4 was found as the most efficient sludge:waste ratio which was also the highest ratio possible.

   This ratio was selected according to the EPA Report of "Municipal Sludge Landfill" that recommended the bulking ratio for the sludge solids content of the sludge used at the study as 4 tons of refuse:1 wet ton sludge (23) and also according to the work of Craft and Blakey that gave the highest sludge to waste ratio to be adopted in operational practices as 1:4.1 (24).

   However, it was stated in the EPA Report that in any event, determinations should be made on a site-by-site basis using test operations (23). Moreover the same report classifies the anaerobically digested sludges as "marginally suitable" in its classification for the suitability of the sludges due to operational problems (23). Therefore such a high ratio may not be adaptable due to operational reasons.

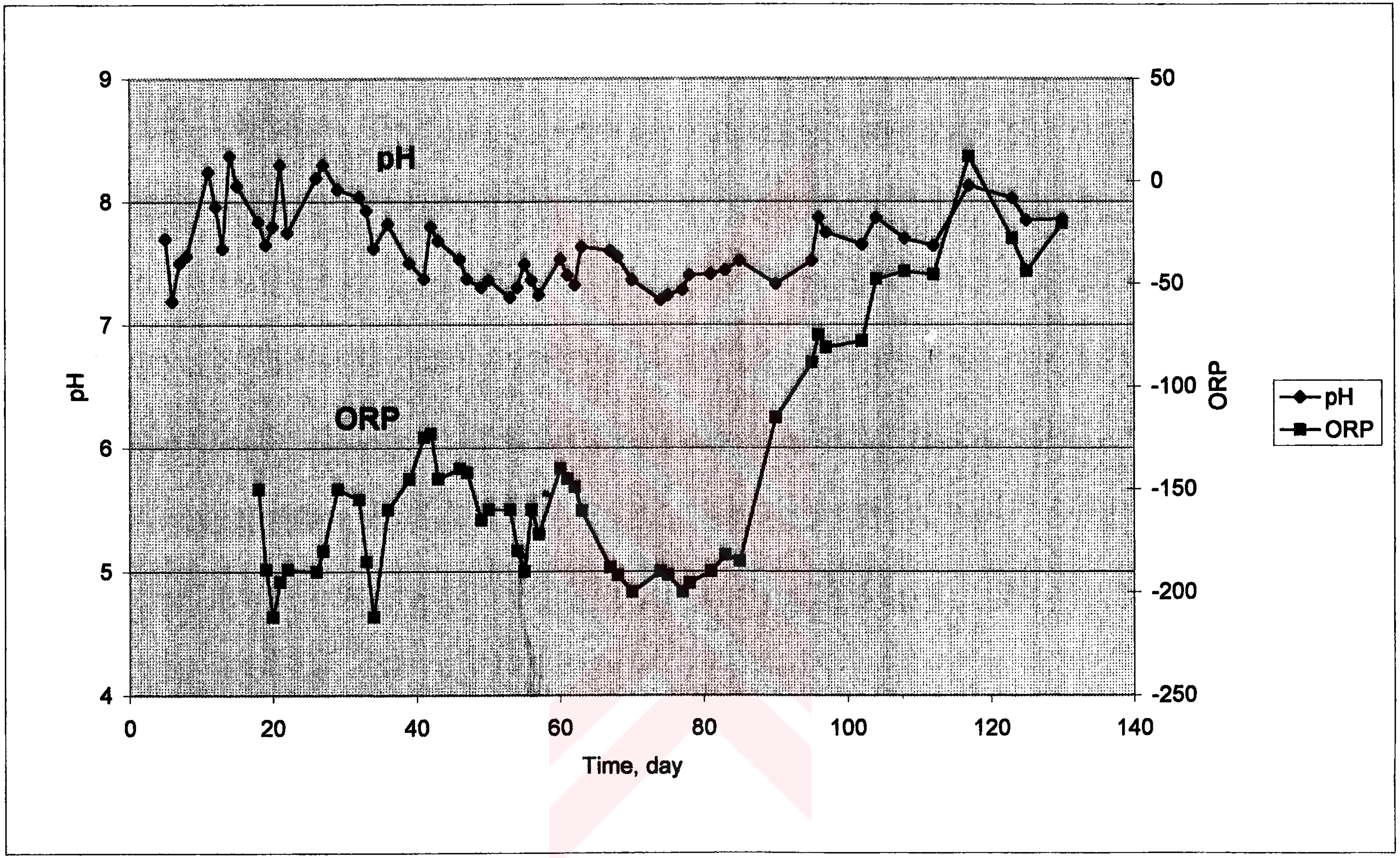

Figure 5.1. pH and the ORP of the Leachate from Reactor 4

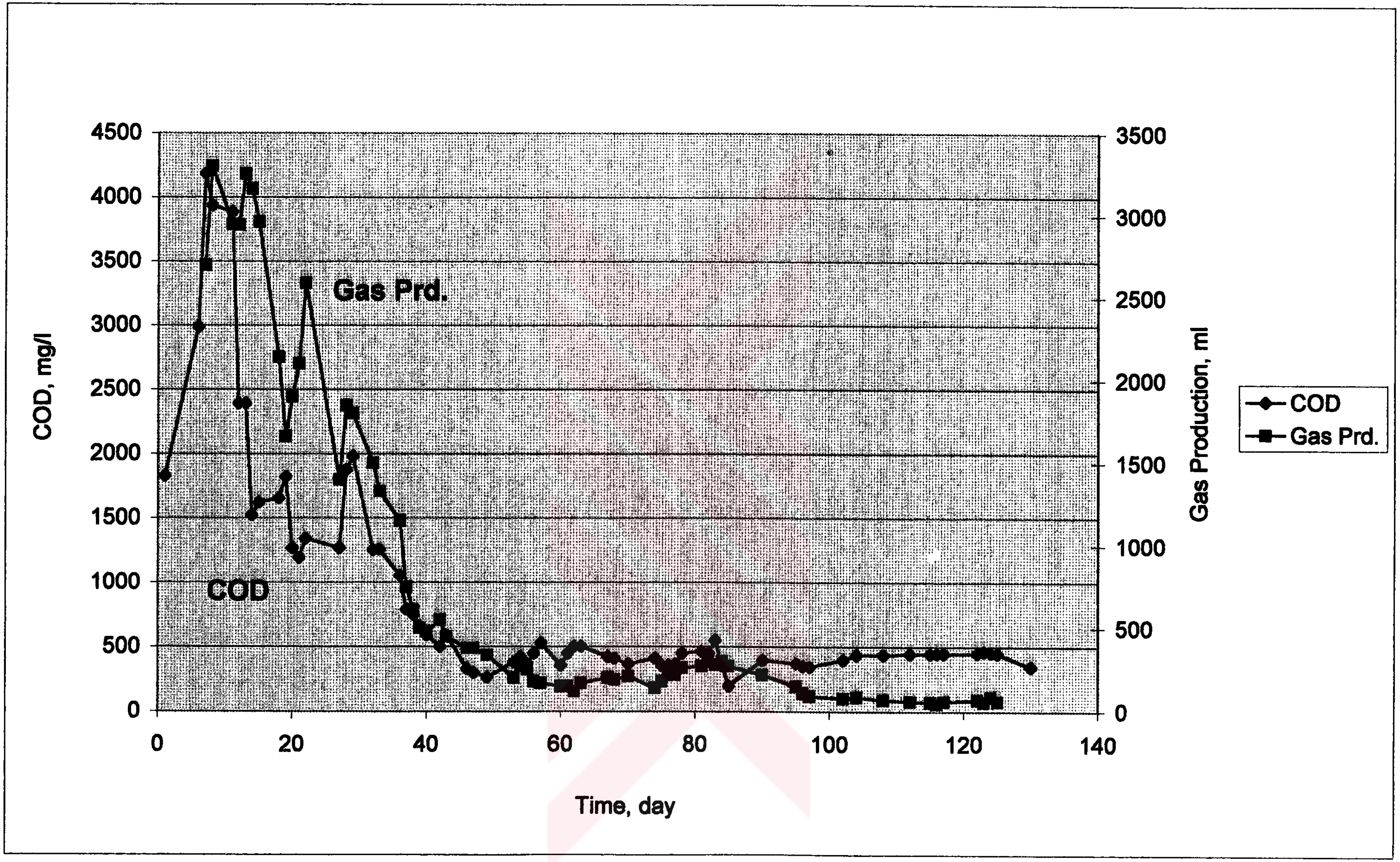

Figure 5.2. COD and the Daily Gas Production of the Leachate from Reactor 4

As a conclusion; for the codisposal, 1:4 sludge to waste ratio was found the most efficient ratio for the stabilization of solid waste. However, the ratio that would be used in the full-scale application can only be determined after test operations due to the possible operational problems. In such a case, the highest ratio that can be used should be selected as the sludge:waste ratio.

6. It was stated that the studies on the remaining stabilization potential could give beneficial results concerning the ultimate disposal option of the site. However, due to the dimension of this study that was limited to one location and one depth, any conclusions could not be made about the remaining stabilization potential of the whole site and therefore, any recommendations can not be made about the ultimate disposal option of the whole site.

7. The main objective of the study was the determination of the remaining stabilization potential of landfilled solid waste. For this determination; the unit used was the volume of methane (CH_4) generated for every kg of solid waste like in many of the similar studies.

   In order to determine the remaining stabilization potential, total gas production potential should be measured or estimated. In this study, it was not possible to measure it because the solid waste used was partially stabilized landfilled solid waste. Therefore, a theoretical gas yield is estimated using the biodegradability approach like in the work of Nynns and Gendebien (30). This approach was preferred to stoichiometric method because of two reasons; first of all, a representative formula of the solid waste used in the study was not known, secondly the biodegradability approach takes the extent of biodegradability into consideration which makes it more realistic. However, it should also be stated that this approach uses some values obtained form the stoichiometric method.

   When using this approach, the moisture content and the percent of biodegradability obtained from this study were used. The specific COD value and the amount of methane generated per gr of COD were taken form the Nynns and Gendebien's work (30). These used values are given in Table 5.1. The theoretical methane yield was estimated as follows;

Table 5.1. The Values Used in the Estimation of Theoretical Methane Yield

Parameter	Used Value	Reference
Moisture Content	45 %	Moisture Analysis of Solid Waste Used
Biodegradability	80%	COD Data of the Study (From the Residual Percentage)
COD Value	1.2 gr COD/dry organic matter	Nynns and Gendebien (1993)
Methane Yield	0.35 l	Nynns and Gendebien (1993)

According to these figures;

1 tonne of municipal solid waste=

$$10^6 \text{ gr x } (1-0.45) \frac{\text{g dry weight}}{\text{g wet weight}} \text{ x } 0.80 \frac{\text{g organic weight}}{\text{g dry weight}} \text{ x } 1.2 \frac{\text{g COD}}{\text{g organic matter}} = 0.528 \text{ x } 10^6 \text{ g COD}$$

$$1 \text{ gr COD}_{\text{organic matter}} = 0.35 \text{ l } CH_4 \text{ at } 0\ ^{\circ}\text{C and 1 bar}$$

By using this assumption;

$$Y_{\text{methane/kg solid waste}} = 0.528 \text{ x } 10^6 \text{ g COD x } \frac{0.35 \text{ lt CH4}}{\text{gr COD}_{\text{organic matter}}} = 184{,}800 \text{ l/ ton solid waste}$$

$$Y_{\text{methane/kg solid waste}} = 185 \text{ l } CH_4\text{/kg solid waste}$$

This yield is also acceptable when the theoretical yields found by using the stoiciometric method in the range of 200-300 l CH_4/kg solid waste are considered. The remaining stabilization potential of the retrieved solid waste was analyzed according to this estimated yield; namely, 185 l CH_4/kg solid waste.

Besides this theoretical yield, the methane yield obtained in the reactors throughout the study is used for the determination of remaining stabilization potential. The total volume of methane production in Reactor 1, 2, 3 and 4 are 19057.5 ml, 15921.2 ml, 17809.34 ml and 22811.8 ml., respectively. The methane generation per kg of solid waste is given in the following table;

Table 5.2. Methane Yields in the Reactor

Reactor	Methane Yield (l CH_4/kg solid waste)
Reactor 1	12.73
Reactor 2	10.61
Reactor 3	11.87
Reactor 4	15.21

The average methane generation is estimated as 12.61 l CH_4/kg solid waste. When this yield was compared with the theoretical yield of 185 l CH_4/kg solid waste, it was seen that only the 7% of the total stabilization potential was remaining in the solid waste when it was retrieved.

Total degradation capacity that was estimated as 7% was a quite low potential. This low value may be due to the low initial COD values. However, there were also some potential errors that caused such a low remaining potential. The most important source of error was the insufficient capacity of the gas collection units. The gas collection units were found full most of the days; on these days the actual gas production could not be determined and the capacity of the unit was taken as the daily production. Therefore the actual gas productions were probably higher than the recorded values. Some errors in the gas composition readings might also be a source of error.

However, a low potential was also expected due to the low initial COD values showing that the retrieved solid waste was already stabilized to an extent. As it was known, no landfill management techniques were operated for the site. The stabilization for the location where the solid waste was retrieved could be attributed to the high moisture content (about 45 %) of the region that accelerated the stabilization. It was also possible that the organic content of that location was already low.

As a conclusion, the remaining stabilization potential of the solid waste was found less that 10%. However, this stabilization potential could not be generalized for the whole site. Even the waste was taken from one location mainly two different ranges initial COD values of 2000 and 7000 mg/l were obtained. This displayed the heterogeneity of the landfill. Because in a heterogeneous mixed-media system such as the one found in a landfill, it was to be expected that may microenvironments, exhibiting varied conditions, might be formed at different locations within the refuse.

In order to determine the stabilization potential of the whole site, this study should be enlarged and the same analysis should be performed for different locations and depths of solid waste until the whole picture of the site was obtained.

6. RECOMMENDATIONS

The scope of the study was limited to specify the technique to be used for the determination of the remaining stabilization potential of the solid waste in landfill. Pilot scale and full-scale studies should be conducted. The representative solid waste samples taken from various locations and depths at the site should be used in these studies to have a general understanding about the solid waste stabilization at the site.

In this study, the solid waste was taken from one location. Despite of this, two different initial COD ranges were obtained in the solid waste used for the study. This created difficulties for the comparison of the findings. Therefore, obtaining representative samples and performing chemical analysis prior to loading are important issues for future studies.

Studying different kinds of sludge and sludge:waste ratios can also be beneficial for the understanding of the extent of stabilization and also for the attempts of alternative sludge disposal options.

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