PRODUCTION OF CERAMIC TILES BY USING MARINE SLUDGE ADDITIVES

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ABSTRACT

PRODUCTION OF CERAMIC TILES BY USING MARINE SLUDGE ADDITIVES

The harbour sediment accumulated in time in the İzmir Bay was investigated by a number of researchers from various aspects. These sediments called marine sludge in this thesis contain organics and heavy metals which pose an important environmental problem. Marine sludge removed from the harbor is required to be safely kept in some form.

In this thesis, production of ceramic tiles by using marine sludge additives was investigated. The sludge is regarded as a suitable raw material for ceramic tile production because of its physical properties and chemical composition. After the sludge is removed from the harbor floor, it was subjected to a series of treatments such as washing, sieving, dewatering, drying and grinding. This treated marine sludge was pressed in the form of pellets and sintered in the 1000-1100 °C range. The treated, untreated and sintered marine sludge along with the separated shells present in marine sludge were characterized by a variety of techniques such as XRD, FTIR, and SEM-EDX.

Marine sludge powders at different proportions (0-50 %) were blended via incorporation into a structural ceramic tile raw material. The mixtures were compressed, and then pellets were fired at temperatures in the 1000-1200 °C range with one-hour hold with a firing rate of 10 °C/min. The products were characterized for mechanical and microstructural properties. Marine sludge added tiles were observed to have higher compressive strength after firing at 1100 °C. The sludge addition caused a lower firing temperature for densification/vitrification of the pellets with higher pore content. Their densities and water absorption values were determined. The densities and water absorption of the tiles fired at 1100 °C was observed to decrease with increasing sludge addition. Leaching tests were performed by varying the leach solution pH and ground tile particle size for chemical durability of the products in the final part of the work. The leaching data have shown that heavy metals were immobilized in the vitrified ceramic structure. The results of this work indicated that blending marine sludge in to the ceramic powder mixtures in the 20-50% range was beneficial for tile production.

ÖZET

DENİZ ÇAMURU İLAVESİYLE FAYANS ÜRETİLMESİ

İzmir körfezinde zamanla birikmiş olan liman çökeltileri birçok araştırmacı tarafından çeşitli metotlarla araştırılmıştır. Organik bileşikler ve ağır metaller içeren ve bu tezde deniz çamuru olarak adlandırılan bu çökeltiler önemli bir çevre problemi oluşturmaktadır. Limandan çıkarılan bu deniz çamuru güvenli bir forma getirilmelidir.

Bu tezde deniz çamurunun fayans üretiminde katkı olarak kullanılması araştırılmıştır. Fiziksel özellikleri ve kimyasal bileşimi itibariyle deniz çamuruna seramik üretimine elverişli hammadde gözüyle bakılmaktadır. Deniz çamuruna liman tabanından çıkartıldıktan sonra yıkama, eleme, susuzlaştırma, kurutma ve öğütme gibi bir dizi işlemler uygulanmıştır. Daha sonra bu işlenmiş deniz çamuru sıkıştırılıp pelet haline getirilmiş ve 1000-1100 °C farklı sıcaklık aralıklarında sinterlenmiştir. İşlenmiş, işlenmemiş, sinterlenmiş deniz çamuru ve çamur içindeki deniz kabukları, XRD, FTIR ve SEM-EDX gibi tekniklerle karakterize edilmiştir.

Deniz çamuru tozları çeşitli oranlarda (% 0-50) fayans hammaddesi (masse) ile karıştırılmıştır. Bu karışımlar sıkıştırılarak pelet haline getirilmiş ve bir saatlik pişme süresi, 10 °C/dk. pişme hızıyla, 1000-1200 °C' de farklı sıcaklık aralıklarında pişirilmiştir. Bu ürünler mekanik ve mikro yapısı bakımından karakterize edilmiştir. Deniz çamuru ilaveli fayansların 1100 °C pişme sıcaklığında daha yüksek basma mukavemetinine sahip olduğu gözlemlenmiştir. Çamur ilavesinin ürünlere daha düşük sıcaklıkta vitrifiye olma özelliği sağladığı fakat daha fazla gözenek içerdiği görülmüştür. Yoğunlukları ve su absorpsiyonu değerleri ölçülmüştür. 1100 °C pişen fayans numunelerinin yoğunluk ve su absorpsiyonu değerlerinin deniz çamuru ilavesinin artması ile azaldığı tespit edilmiştir. Ayrıca pH değeri ve tane boyutu parametreleri ile ürünlerin kimyasal dayanıklılığını ölçmek için özümleme (liç etme) testi uygulanmıştır. Ağır metallerin vitrifiye seramik yapı içerinde hapsolarak ayrılmaz bir hale geldiğini özümleme (liç etme) testi sonuçları göstermiştir. Bu çalışmanın sonuçları gösteriyor ki % 20-50 aralığında seramik toz karışımlarına deniz çamuru ilavesi fayans üretimi için fayda sağlamıştır.

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CHAPTER 1

INTRODUCTION

İzmir bay has been fed with large amounts of sediments through streams for a long period of time. Disturbing (also poisoning) odor from the bay caused by odorous air pollutants, such as hydrogen sulfide and sulfur containing organic compounds (Müezzinoğlu, 2003) polluted the city and İzmir Bay severely for a long time. The analysis of some fish species rambling in depth of the bay affected highly with dissolved and undissolved heavy metals can be used as indicator (Küçüksezgin et al., 2005a) of this pollution. Sediment formation started as a result of this pollution. This sediment contains harmful heavy metals and organics which are dangerous for human and marine organisms. About 6.000.000 m^3 of material can be dredged from İzmir Bay according to preliminary evaluations (Özerler et al., 2005). These sediments (marine sludge) that contain organics and heavy metals settled in the sea floor poses a real problem for both environment and harbor operations. The sludge has been regularly removed from the harbor floor by excavation to create room for large tonnage ships to safely dock in the harbor. The sludge removed from the harbor must be safely kept in some form.

The sediment is regarded as a suitable raw material for brick production because of its perpetual availability, homogeneity and mineralogical and chemical composition (Hamer and Karius, 2002). The use of the sediment as a clay mixture in brick manufacturing seemed possible up to 40 percent (Karpuzcu et al., 1996). There is a factory named Hanseaten-Stein Brickworks located near Hamburg which produces brick from dredged material (Hamer and Karius, 2002). Ceramic materials with good mechanical properties which were produced by using powders obtained from calcined dredged spoils alone were found to be able to immobilize most of the hazardous elements contained in the starting materials (Baruzzo et al., 2006). According to the study by Giese et al., the sludge dredged from İzmir Bay can be used up to 50 % in brick production and the produced brick containing 50 % sludge additives by weight presented usable ceramic properties (Giese et al., 2003). The motivation behind this work which was inspired by the results of the above study was on the use of marine sludge in ceramic production where environmentally hazardous chemicals would be immobilized within a vitrified ceramic body. The targeted ceramic could be a tile or a brick. Although extensive research have been conducted on the use of sludge in brick production, studies on the sludge-containing tile production is limited.

The floors, bathrooms and kitchen of our houses that are essential in our daily life become useful and beautiful with ceramic tiles. The scope of this thesis involves the use of marine sludge for ceramic tile production. This sludge use is expected to lead to beneficial products while decreasing the cost of tile production due to lower firing temperatures. The safe disposal of an environmentally polluting material is an added major advantage of this sludge use in tile production to the society. This use necessitates additional pretreatment processes like the removal of shells and salts present in the sludge. The cleaning of harbor in order to increase the harbor depth to maintain an adequate shipping channel for the arrival of special ships is also a necessity for safer harbor operations. The cost of cleaning harbor may also decrease if the use of sludge in tile production decreases the production cost.

This thesis contains the following subjects. Marine pollution in İzmir Bay and utilization of sludge in various applications are reviewed in the Chapter 2. In Chapter 3, ceramic tile and its historical background, ceramic tile sectors in Turkey, ceramic tile raw materials, ceramic tile processing, the use of marine and other sludge in ceramic industry and characterization of ceramics are presented. The experimental methods and the results of this work are presented and discussed in Chapters 4 and 5. The last chapter briefly states the conclusions of this work and recommendations for future work.

CHAPTER 2

THE UTILIZATION OF MARINE AND SEWAGE SLUDGE

In this chapter, marine pollution in İzmir bay and utilization of sludge and various applications will be briefly explained.

2.1. Marine Pollution in İzmir Bay

İzmir, one of the largest city in Turkey, is located at the eastern end of İzmir Bay and it has one of the biggest harbors in Turkey. İzmir Bay is located in the eastern Aegean Sea between latitudes of 38° 20′, 38°42′ N and longitudes of 29°25′-27°10′ E. The bay has a total surface area of over 500 km^2, water capacity of 11.5 billion m^3, a total length of 64 km and opens in the Aegean Sea. The depth of water in the outer bay is about 70 m and decreases towards to the Inner Bay. The bay has been divided into three sections (outer, middle and inner) according to the physical characteristics of the different water masses.

İzmir has some environmental problems as every rapidly growing city. One of the problems is marine pollution. Untreated industrial and domestic wastewater had been discharged to İzmir Bay until the wastewater treatment plant began operation in early 2000. Disturbing (also poisoning) odor rises from the bay as a result of odorous air anaerobic reaction and resulted in emissions of hydrogen sulfide and sulfur containing organic compounds such as methane thiol, ethane thiol, 2-propane thiol, 2-butane thiol, dimethylsulfide, dimethyldisulfide, thiophene, diphenylsulfide (Müezzinoğlu, 2003). Although the capacity of wastewater plant (WTP) is sufficient for removal of nitrogen from the wastes, but the WTP is not adequate to remove phosphate. The quality of the marine environment in the middle and inner parts of the bay has not yet noticeably improved. There were no significant differences that were detected in the overall average values of nutrient concentrations between the samples collected before and after WTP became operative (Kontas et al., 2004). Nevertheless, İzmir Municipality plans to collect all discharging wastewater in a channel and after treatment to discharge it to the

Middle Bay. This means that in the future the Inner Bay water will be replaced with water which has a considerable higher quality after the waste water treatment has been achieved (Sayın, 2003). In dredging sludge from İzmir Bay, sulfur, oil-grease, phosphorus and heavy metal concentrations are very high. These high concentrations are the result of untreated wastewater discharged to the Melez and Arap Rivers from settlement and industrial regions (Filibeli et al., 1995). They affect benthic flora and fauna negatively when they are disposed to deep water.

This is usual to increase marine pollution by heavy metal and hydrocarbon because the main industries in İzmir region include food processing, oil, soap and paint production, chemical industries, paper and pulp factories, textile industries and metal processing, This problem has been showed that metal concentrations ranged between Hg: 0.05-1.3, Cd: 0.005-0.82, Pb: 14-113 and Cr: 29-316 µg/g in the sediments and significant enrichments were mostly found in Inner Bay (Küçüksezgin et al., 2005a). Outer and middle bays show low levels of heavy metal enrichments except estuary of Gediz River. The concentrations of Hg, Cd and Pb in the outer bay were generally similar to the background levels from the Mediterranean. The highest total hydrocarbon levels were found in the inner bay due to the anthropogenic activities, mainly combustion processes of traffic and industrial activities.

Some kind of fishes that live in depth of İzmir Bay such as Red mullet *(Mullus barbatus)*, red Pandora *(Pagellus erythrinus)*, hake *(Merluccius merluccius)*, annular sea bream *(Diplodus annularis)* and common sole *(Solea vulgaris)* can be used as an indicator of marine pollution by heavy metal because these fishes ramble in depth of the bay and they are highly related to dissolved and undissolved heavy metal in marine water. The concentrations of heavy metals found in fish varied for Hg: 4.5-520, Cd: 0.10-10 and Pb: 0.10-491 µg/kg in Izmir Bay (Küçüksezgin et al., 2005a). A person can consume more than 2, 133 and 20 meals per week of fish in human diet would represent the tolerable weekly intake of mercury, cadmium and lead, respectively, in İzmir Bay.

The overall order of the metal concentrations found in fish species was: Pb > Hg > Cd (Küçüksezgin et al., 2005b). Maximum permitted Hg concentrations in marine organisms for the majority of Mediterranean countries lie between 0.5 and 0.7 µg/g wet weight. The maximum value of Hg detected was 829 µg/kg for the edible parts of fish. Consumption of 360 g of such fish per week represents the maximum tolerable for human consumption (300 µg mercury per week per 60 kg human). Similarly, the provisionally tolerable weekly intake of Cd has been estimated to be 400-500 µg per person per week. The maximum value of Cd in this study was 10 µg/kg, and a person could, therefore, consume more than 150 meals of fish per week. The maximum concentration of Pb in fish observed was 943 µg/kg. Consumption of 10 meals per week of this fish represents the tolerable weekly intake of lead (3000 µg lead per 60 kg human). Trace metal concentrations found were higher than those from clean areas of Aegean and Mediterranean Sea, and are likely due to natural and industrial inputs to Izmir Bay (Küçüksezgin et al., 2005b). On the other hand, metal concentrations in Izmir Bay are considerably lower than those found in polluted areas of Mediterranean Sea. Inner and Middle Bays of Izmir Bay are also highly contaminated with organic pollutants (Arınç et al., 1999).

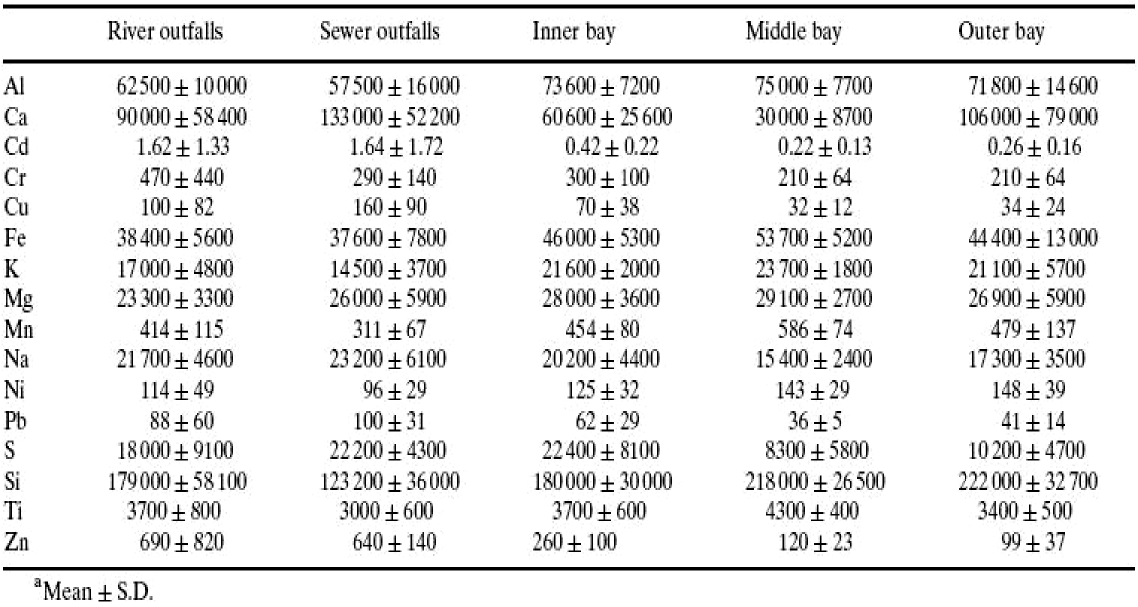
One of the most important sources for marine pollution is Aliağa which is a town of İzmir. The Aliağa (İzmir, Turkey) area is situated in Western Anatolia. The steel industry in Aliağa City, 50 km north of İzmir on the Aegean Coastline of Turkey, is causing heavy-metal pollution in the area. Many iron smelters and roller mills were built in the southwest of the Aliağa City.

The concentration of Pb, Cd, Zn, Cr, Mn, and Fe in the plants, soil, and air were found to exceed the limit concentrations within 2.5 km to the steel plant between 1996 and 1997 (Sponza et al., 2002). Generally, the heavy-metal level decreases by increasing of depth. The heavy-metal levels increased significantly with the years. The heavy-metal concentrations decreased sharply with the distance from the still mill. The air quality standards in the surrounding of metal industry is higher than those obtained in industrial areas in terms of particulate matters containing Fe, Zn, Pb, and Cu according to Air Pollution Prevention Regulation. The drinking water related to the metal industry area must not be used as drinking water due to fecal coliform, Pb, and Cu contamination. The river water containing the wastewater of the metal industry is polluted and must not be used as irrigation water.

The chemical composition of particulate matter in İzmir Bay chances season by season. It has been determined and evaluated together with the hydrographic features, chlorophyll-a and dissolved inorganic nutrient, and dissolved organic carbon data in the Izmir Bay (Küçüksezgin et al., 2005c). Particulate concentrations were low during the less productive winter period when the water column was enriched with dissolved inorganic nutrients in the Izmir bay. The highest particulate concentrations were observed in the March period, while DOC (dissolved organic carbon) concentrations were low in the water column, accompanied by apparent decreases in the water transparency in the outer part of the bay. The particulate matter concentrations decreased markedly below the surface waters to low levels, which may have been due to effective removal of photosynthetic particles by rapid sedimentation.

İzmir Bay was highly polluted and also in the bottom of the bay, therefore sediment formation started. This sediment includes in harmful heavy metal and organics which are dangerous for human and marine organism. 6.000.000 m^3 material could be dredged according to preliminary evaluations (Özerler et al., 2005). Although the bay is polluted with heavy metal, a metal may require marine life like iron. It has ecological significance both in the open ocean and coastal waters. The enrichment of iron and its speciation have an impact on coastal ecology (Öztürk et al., 2003). Heavy metal contaminant can be seen from Table 2.1.1.

Table 2.1.1. Average concentrations of elements in river outfalls, sewer outfalls and different parts of the bay measured by AAS and XRF ($\mu g.g^{-1}$) (Source: Atgın et al., 2000).



	River outfalls	Sewer outfalls	Inner bay	Middle bay	Outer bay
Al	62500 ± 10000	57500 ± 16000	73600 ± 7200	75000 ± 7700	71800 ± 14600
Ca	90000 ± 58400	133000 ± 52200	60600 ± 25600	30000 ± 8700	106000 ± 79000
Cd	1.62 ± 1.33	1.64 ± 1.72	0.42 ± 0.22	0.22 ± 0.13	0.26 ± 0.16
Cr	470 ± 440	290 ± 140	300 ± 100	210 ± 64	210 ± 64
Cu	100 ± 82	160 ± 90	70 ± 38	32 ± 12	34 ± 24
Fe	38400 ± 5600	37600 ± 7800	46000 ± 5300	53700 ± 5200	44400 ± 13000
K	17000 ± 4800	14500 ± 3700	21600 ± 2000	23700 ± 1800	21100 ± 5700
Mg	23300 ± 3300	26000 ± 5900	28000 ± 3600	29100 ± 2700	26900 ± 5900
Mn	414 ± 115	311 ± 67	454 ± 80	586 ± 74	479 ± 137
Na	21700 ± 4600	23200 ± 6100	20200 ± 4400	15400 ± 2400	17300 ± 3500
Ni	114 ± 49	96 ± 29	125 ± 32	143 ± 29	148 ± 39
Pb	88 ± 60	100 ± 31	62 ± 29	36 ± 5	41 ± 14
S	18000 ± 9100	22200 ± 4300	22400 ± 8100	8300 ± 5800	10200 ± 4700
Si	179000 ± 58100	123200 ± 36000	180000 ± 30000	218000 ± 26500	222000 ± 32700
Ti	3700 ± 800	3000 ± 600	3700 ± 600	4300 ± 400	3400 ± 500
Zn	690 ± 820	640 ± 140	260 ± 100	120 ± 23	99 ± 37

[a] Mean ± S.D.

A study searched on heavy metal source in İzmir Bay, heavy metal contaminant and technique for analyzing heavy metal in sludge presents that Cd is known to be rich in fly ash discharged to the marine environment, discharges from alloy producing and ceramic plants, Cr is enriched in discharges from tanneries, textile and metal production, Cu is discharged particularly from metal plating and glass producing plants, Pb is a good indicator of traffic-related sources or battery recycling plants, Ni is discharged from the metal plating industry, S is rich in fly ash and discharges from petroleum processing, Zn is enriched in discharges from various industries such as tanneries, paint and metal plating. Mercury is an excellent tracer for paper production. Litophilic elements such as Al, Si, Sc, Fe, Co, rare-earths can be used to identify natural sediment matrix components (Atgın et al., 2000). Figure 2.1.1. shows that degree of contamination in İzmir Bay surface sediments caused by the following 12 metals: Ag, Cd, Cr, Cu, Hg, Mo, Pb, Sb, Sn, V and Zn (Duman et al., 2004).

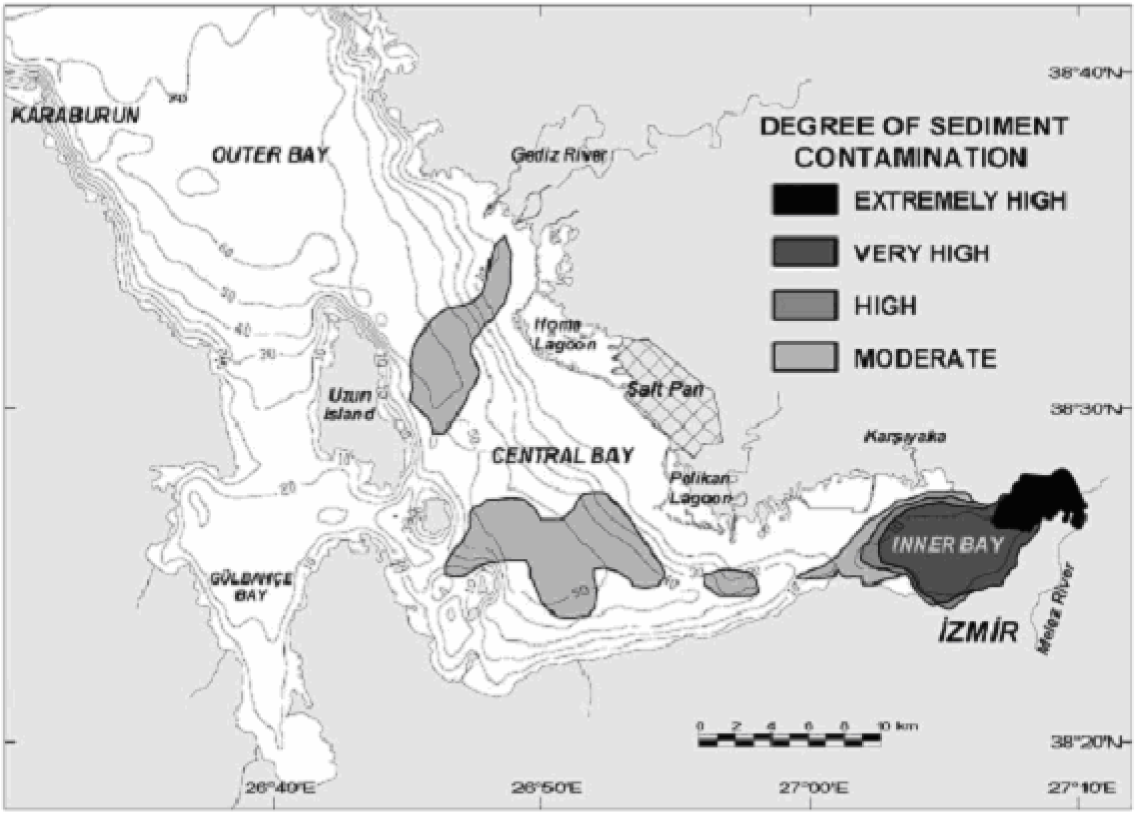


Figure 2.1.1. The map showing degree of contamination in İzmir Bay surface sediments caused by the following 12 metals: Ag, Cd, Cr, Cu, Hg, Mo, Pb, Sb, Sn, V and Zn (Source: Duman et al., 2004).

Moderate levels of heavy metal contamination are around the Hekim Island Dump Site due to probably caused by the continuous dumping of sediments excavated from the most polluted innermost Inner İzmir Bay between 1976 and 1990(Aksu et al., 1997). Inner İzmir Bay surface sediments also contain very high heavy metal toxicities, with values dramatically decreasing at the Yenikale Entrance as in shown figure 2.1.2.

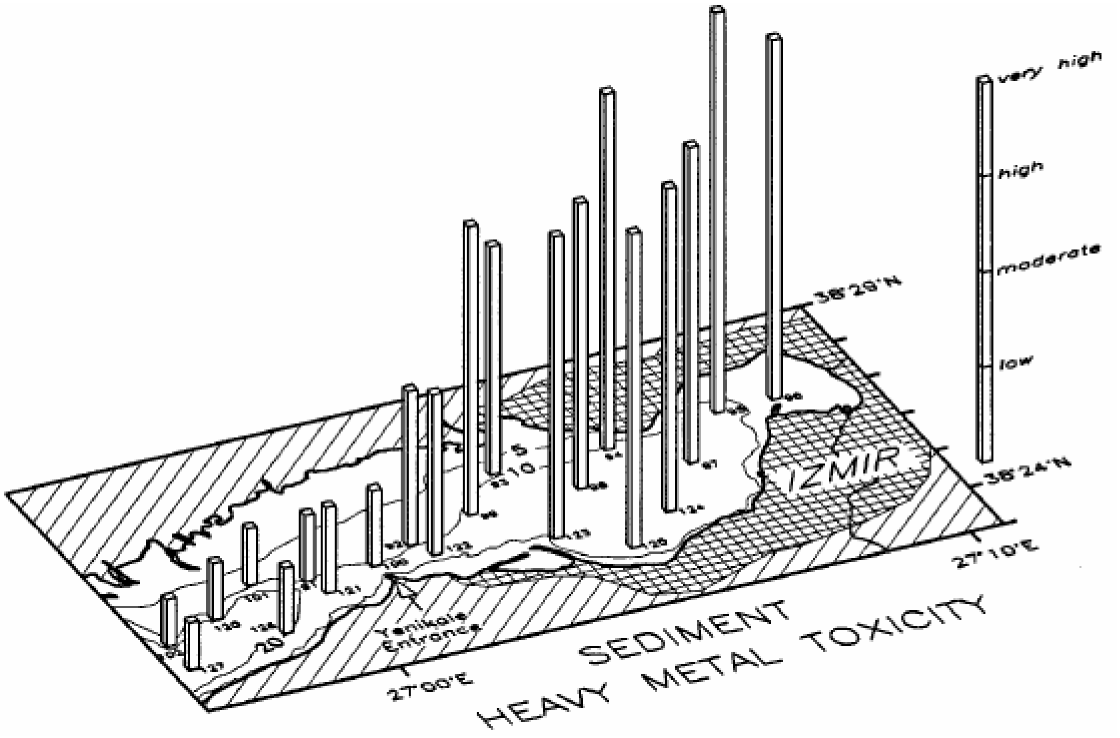


Figure 2.1.2. Heavy metal toxicity values in the Central and Inner İzmir Bay surface sediments (Source: Aksu et al., 1997).

On the other hand, Aegean Region of Turkey consists of numerous Hg deposits in Karaburun, Bayındir, Tire, Ödemis, Alasehir, Ulubey, and Banaz districts from which approximately 5500 t of mercury have been produced. Groundwater and rivers have been polluted with mercury and other heavy metals such as As, Sb, Ni and Cr (Gemici et al., 2003).

In this case, mentioning about distribution of the surficial element in İzmir Bay could become useful. Bottom sediments are relatively coarse in the west, with a general fining towards to the east in the outer part of the bay. This fining pattern is reversed in the inner bay (Figure 2.1.3). Sand and sandy materials with mean grain sizes 2.8–3.7 diameter (Figure 2.1.3) are located near the northwest shore of the outer bay and the shallow water pro-delta deposits encircling the shores of the present-day Gediz delta at the west of the salt-pan area in the central bay (Figure 2.1.3). Two large barrier islands surrounding the Homa and Pelikan lagoons and several smaller sand bars are also composed of moderately sorted sands, and are formed through winnowing and reworking of progradational channel mouth deposits by waves and long-shore currents following delta abandonment (Figure 2.1.3).

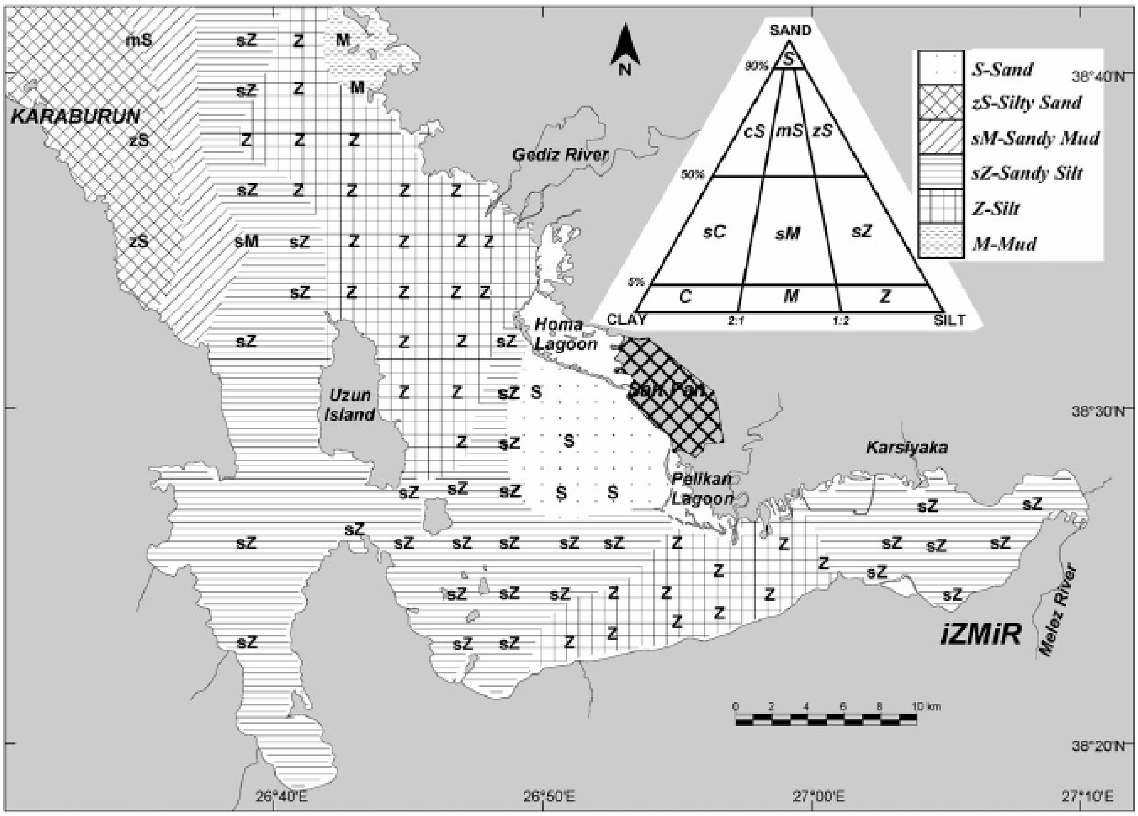


Figure 2.1.3. Map showing distribution of surficial sediments in İzmir Bay (Source. Duman et al., 2004).

Sandy silts with mean grain sizes of 5–7 diameter are present in most of the western half of the outer bay and the eastern end of the inner bay. In the eastern half of the outer part of bay and the west of the inner bay, silt is the major component of the sediments. In the deepest part of the eastern side of the outer bay, however, mud is the major component of the sediments (Figure 2.1.3).

Towards the east, from the western part of the Outer İzmir Bay to the Gediz River delta plain, the bottom sediments generally become finer, more poorly sorted and more positively skewed. Coarsening of sediments, accompanied by better sorting and increasing negative skewness, have been observed in the east of central bay (Duman et al., 2004). Fine-grained sediment occurs predominantly within the deeper part of the Outer İzmir Bay. Most of the coarse grained sediments are deposited along the higher energy shoreline encircling the Outer and Central İzmir Bay.

The surface sediments ranged between 15.9% and 48.3% (Figure 2.1.4). The carbonate contents falled in the range between 20% and 25%; with the lower (down to 16%) and higher (up to 48%) values being exceptions (Duman et al., 2004). The highest carbonate contents were found in the western part of the central bay, and the lower carbonate values occur within the fine sand in the eastern part of the central bay. Most of the carbonates present in the southwestern part of the bay are associated with the remains of gastropods and bivalves either as a whole skeleton or as smooth convex plates up to 1 cm. In the southwestern part of the bay where the greatest $CaCO_3$ contents were identified, whilst most of the carbonate is of biogenic origin, the remainder is of probably detrital origin, derived from Mesozoic carbonate rocks that are well exposed in the hinterland.

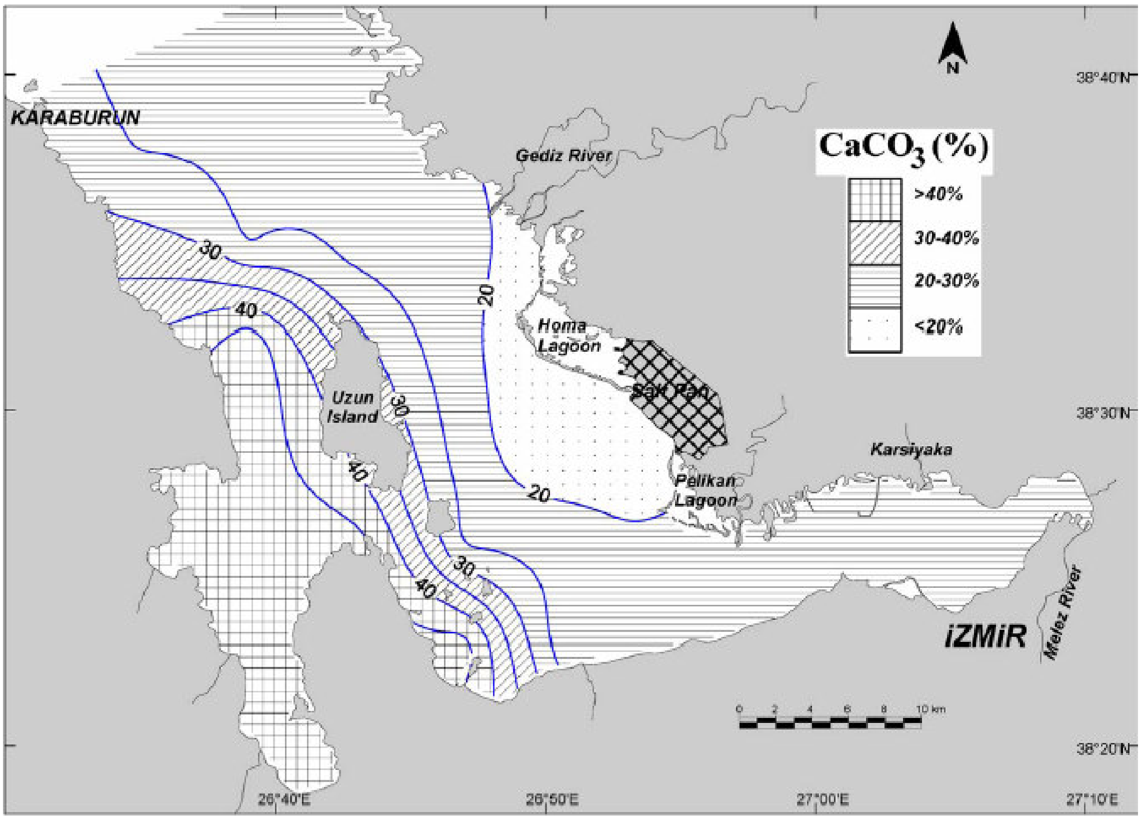


Figure 2.1.4. Distribution map of the total carbonate contents of surface sediments in the İzmir Bay (Source: Duman et al., 2004).

Total organic carbon concentrations of the bottom sediments from the İzmir Bay varied between 0.40% and 3.12% with a general tendency for higher values in silt sized fraction with between 0.5% and 0.8% in the outer bay (Aegean Sea—İzmir Bay approach), 1.0%–1.5% in the central bay and 1.5%–3.1% in (Figure 2.1.5). The distribution of organic carbon in these sediments supports the importance of the influence of pollution. Most of organic materials are retained in silt near the pollutant source (Duman et al., 2004). İzmir harbor, located at the eastern end of the Inner İzmir

Bay receives several raw sewage and industrial outfalls via the Melez River and several streams.

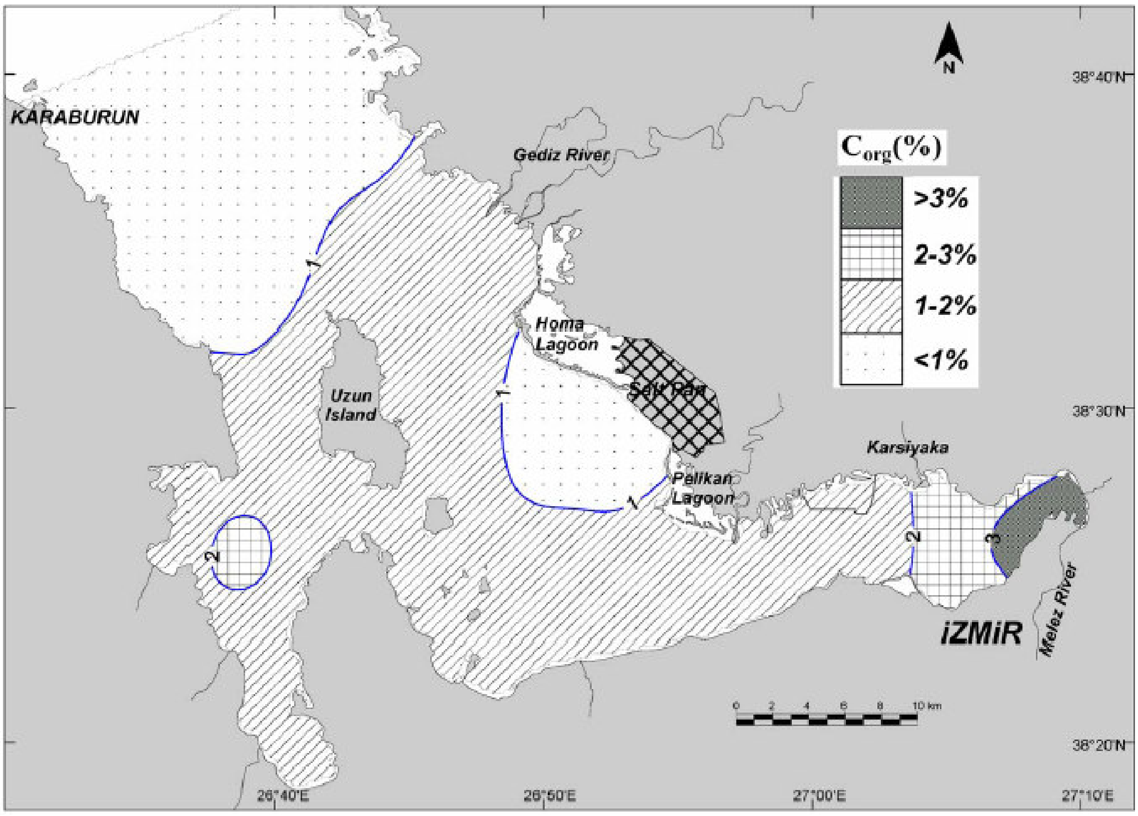


Figure 2.1.5. Distribution map of the total organic carbon of surface sediments in the İzmir Bay (Source: Duman et al., 2004).

Unfortunately, there is another bay undergoing marine pollution like İzmir bay in our country. The Golden horn which was a famous recreational area at the time of Ottomans is a highly used water body in Turkey and also served as the most important port of the region. Golden Horn suffered from heavy pollution due to extensive industrialization and rapid population growth in İstanbul in the twentieth century. This manuscript describes how metal pollution evolved in the Golden Horn between 1912 and 1987, by analyzing ^{210}Pb dated slices of a 3-m long core colleted close to Galata bridge in 1989 (Tuncer et al., 2001). Although anthropogenic elements Mo Zn Cr Cu Ag and Cd account for a minute fraction of the elemental mass, their concentrations increase along the core, signifying human influence on chemical composition of the Golden horn Sediments. Lead was enriched at the bottom of the core suggesting pollution of Golden Horn sediments by this element even at the beginning of the century, but observed concentrations of the remaining anthropogenic elements, at the bottom of the core, can be explained be sedimentary material. Concentrations of pollution-derived elements do not change significantly between 1912 and 1950, but their concentrations increase sharply in the second half of the century. A factor analysis applied to the data set has shown that the inorganic fraction at the Golden Horn sediments includes crustal, marine and two anthropogenic components. One of the anthropogenic components is attributed to the discharges from an iron and steel plant. The second anthropogenic component, which accounted for a larger fraction of system variance, is due to discharges from industries, particularly metalwork plants.

2.2. Utilization of Sludge and Various Applications

Sludge can be defined as the settleable solids separated from liquids during processing; the deposits of foreign materials on the bottoms of streams or other bodies of water (Cheremisinoff, 2002). Contaminated sediments may be treated in-situ or ex-situ. If no in-situ method can be applied, maybe because the sediment must be dredged in order to guarantee a water depth, dredging is necessary and different ex-situ techniques will be compared. Relocation, disposal and treatment with different subsequent uses can be distinguished given in Figure 2.2.1.1 and in the following the general technical concepts and technical as well as environmental feasibility will be considered.

2.2.1. In-situ Treatment Techniques

In-situ methods should minimize the risks posed from sediments towards the environment to an acceptable level and that for a foreseeable long period (Hamer, 2005). In order to control such risks, all processes involved in fate and transport of the chemicals posing the risk to the environment have to be considered.

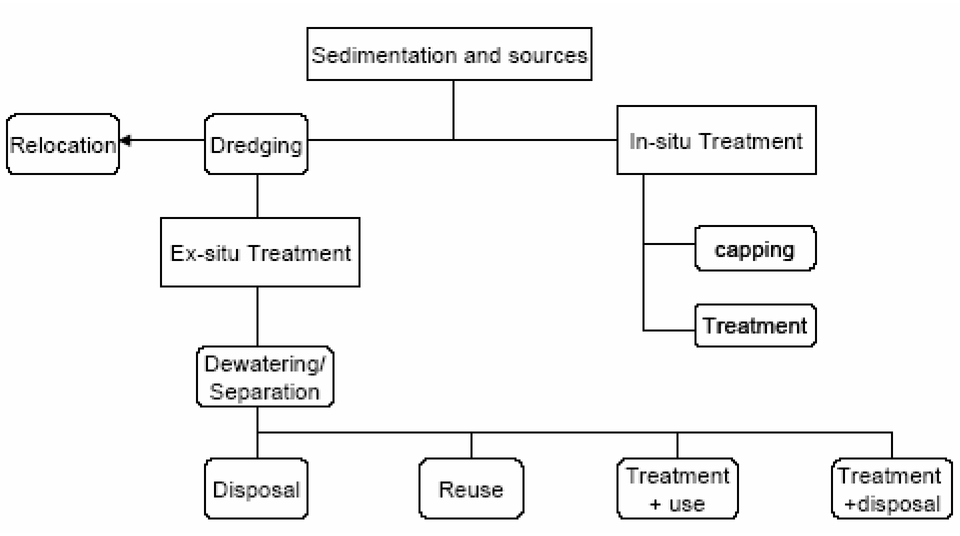


Figure 2.2.1.1. Overview on treatment and disposal techniques
(Soure: Hamer, 2005).

The processes taking place during the treatment procedure can be distinguished in physical, chemical and biological processes. Re-suspension of the sediment caused by bottom-near currents, advection of interstitial water, maybe due to groundwater infiltration and diffusion of dissolved chemicals following a concentration gradient between interstitial water and bottom-near water, dispersion, dilution and at least sedimentation burying older layers can be summed up as the important physical processes.

Organisms which live on or near the sediment surface may contribute to the release of pollutants from the sediments in different ways. The degradation induced by microorganisms as well as bio-irrigation or bioturbation which is the physical mixing of sediment due to the activity of burrowing species are known. Compared with molecular diffusion the effect of bioturbation seems to be negligible. More important is the process of bio-irrigation. These processes can alter the mobility of chemicals and influence the risk posed to the environment. This change can be called aging or natural attenuation. For heavy metals these phenomenon leads to enhanced retention and for organic contaminants to retention, degradation or metabolism. Besides attempts to apply biological and chemical techniques, capping of contaminated sediments is the option which is conducted most.

In-situ biological treatment is based on the idea that additives carrying nutrients, bacteria and oxygen-carrying compounds accelerate the natural process of biological degradation of degradable organic contaminants in the sediments.

Chemical methods try to fix pollutants by forming precipitates such as sulphides or enhance sorption of harmful chemicals and to keep boundary conditions such as pH value and redox-conditions in a way that pollutants are as immobile as possible. However, the assessment of such a strategy, especially on the long term, is complicated because the characterization of binding forms is still on debate and no routine method and the characteristics of the sediment with respect to bonding are strongly dependent on pH- and redox-value. To guarantee such boundary conditions by the exclusive application of chemicals to a sediment in a river or waterway seems to be hardly possible, so that such techniques are not applied in practice. It would be a more promising way to control the important boundary conditions enhancing the retention of pollutants by applying methods like subaqueous disposal, thermal treatment or capping.

It is worth mentioning capping construction which is to prevent mobilisation of the sediment and to reduce the release of pollutants from sediments. A capping construction can consist of one or more layers and in combination with geo-textiles which can have both, a geotechnical and chemical effect. The cap must sufficiently retard the migration of contaminants from the sediment caused by bioirrigation, advection and diffusion. The design of the cap may also include materials to adsorb pollutants migrating with the porewater due to the consolidation process or diffusion

2.2.2. Ex-situ Treatment Techniques

Dredged material can be disposed off into rivers or the sea or stored in up-land or aqueous disposal sites. Other alternatives are the treatment of the dredged sediments in order to improve their chemical or physical properties (Hamer, 2005). End destination might be the substitution of primary resources in different fields or an improved disposal. It can be helpful or necessary to dewater the dredged material and to separate different fractions of the dredged sediments before disposal or treatment.

It is common practice to relocate most of the material back into the river or into the sea in places where the sediment does not disturb shipping and ecosystems because this method is very cost-effective. Aquatic ecosystems can be influenced by relocating theses sediments because of physical and chemical processes. Physically the disposal leads to an increased turbidity in the water column and to a burial of benthic flora and fauna. Chemically relocation is accompanied by an oxygen consumption in the water body on the short term, but with time increasing concentration of nutrients, distribution of pollutants and their enrichment have to be considered.

It is useful here to mention subaquatic disposal techniques. Sediments act like sinks for a wide group of chemicals due to chemical and physical boundary conditions. So it seems to be logical to keep sediment or to dispose contaminated sediments in environments with the same boundary conditions, namely to dispose them under aqueous conditions. Disposal facilities for contaminated dredged material are distinguished 2 types of subaquatic disposal as given in Figure 2.2.2.2: open water disposal, disposal capped with clean material, and artificial islands/nearshore disposal facilities surrounded by a dike.

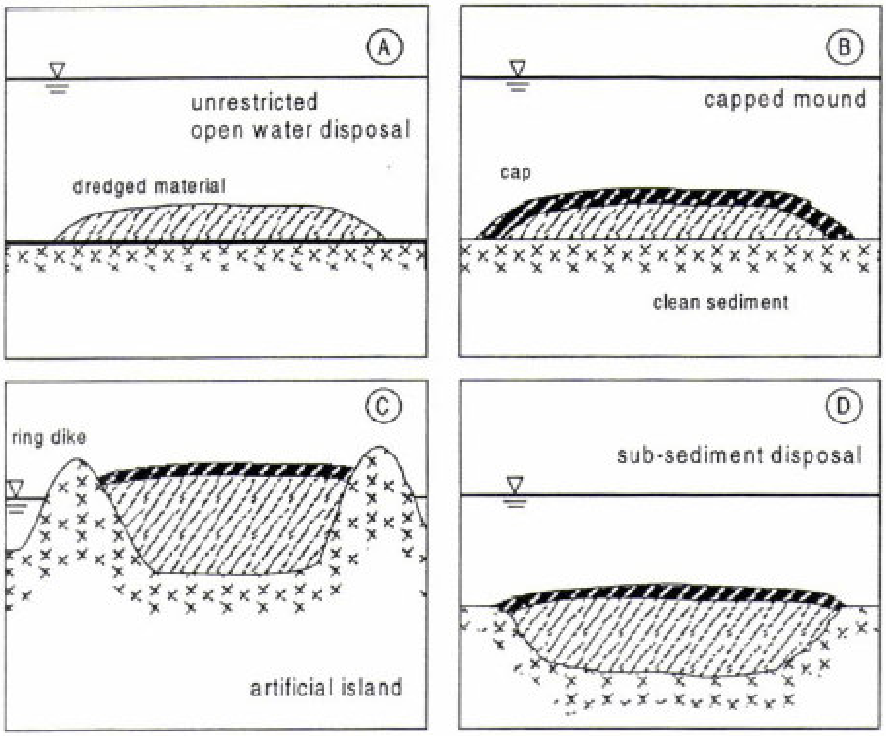


Figure 2.2.2.2. Types of subaqueous disposal for dredged material
(Source: Hamer, 2005).

However, due to dewatering and dry disposal at the atmosphere the geochemistry of the sediments might change completely: Oxidation of reduced chemical species, degradation of organic matter, both maybe accompanied by acidification, volatilization of volatile chemicals or gaseous metabolites might occur. So an upland disposal can lead to new boundary conditions with maybe higher chemical gradients than before dredging or compared to subaqueous disposal. Those increased chemical gradients bear the risk of an increased mobilization on the long term, if capacity controlling properties like acid buffer capacity or sorption capacity are overloaded or consumed.

At the starting point of a bioremediation sediments are anaerobic and in most cases the heavy metals are strongly bound as sulphide or carbonate and organic pollutants are sorbed to the matrix. During the treatment the dredged material becomes aerobic, organic matter is degraded and sulphides are oxidized and moreover the pH can decrease if the buffer capacity of the dredged material is consumed. As a result, the contaminant's mobility as well as the availability for plant uptake or soil living organisms is increased. If these processes are enhanced this enhancement can be called a bioremediation.

Chemical Extraction Techniques use solvents and mechanical actions to remove contaminants. Simple water washing or extraction agents as acids, bases, chelatants, surfactants and reducters can be applied. Disadvantages were high waste water production and destruction of positive soil characteristics of the treated material like dissolution of clay minerals, leaching of nutrients and consumption of complete acid buffer capacity. In case of complexing agent NTA and EDTA were very effective but nearly not degradable and consequently seen as a risk on the environment itself.

2.2.3. Sludge Applications

In general, both marine and sewage sludge have heterogeneous structures (sometimes named matrix structures). Because of having normally is 70% water, sludge can be regarded as gel-like material (Dursun et al., 2005). Figure 2.2.3.1 indicates the SEM images conducted on the digested sludge which supports the matrix structure.

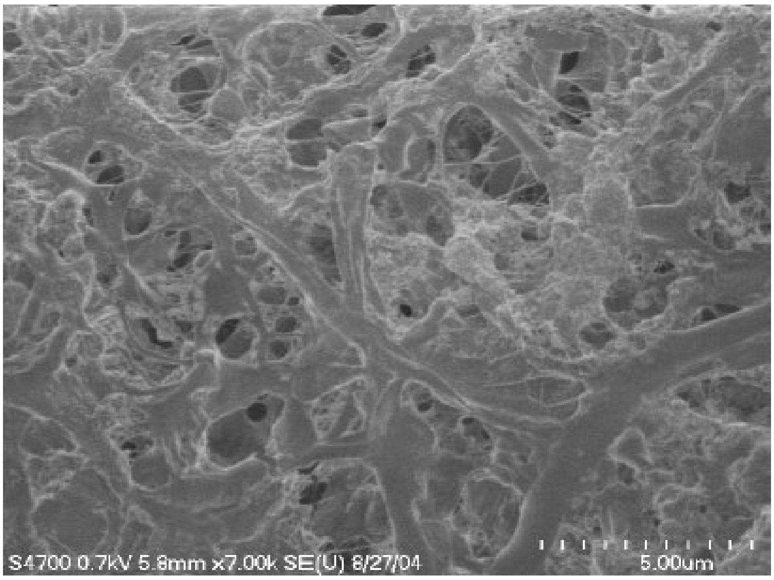


Figure 2.2.3.1: SEM images of digested sludge
(Source: Dursun et al., 2005).

The four sludge disposal methods which are currently used, i.e. recycling in agriculture, landfilling, dumping into sea, and incineration are examined. The future trend presented showing the increasing role of sludge incineration (Werther and Ogada, 1999). The sludge containing potassium, nitrogen and phosphorous, it can be considered as a manure (Tunç et al., 2005), (Yurtsever et al., 2005). The sludge can also increase efficiency of the ground for plant growth (Küçükhemek et al., 2005). Low cost and effective solidification/stabilization techniques for the sludge by using fly ash and natural product clinoptilolit (zeolite) investigated (Kocasoy et al., 2005) and the optimum mixing ratios to obtain a solidified product which has high unconfined compressive strength and low leaching values have been determined.

The field of the engineering interested in construction materials offers opportunities for the use of dewatered and stabilized dredged material (Hamer, 2005). Dredged material is applied in industrial scale: De-watered silty dredged material is used for liners in the confined disposal facilities (CDFs) in Hamburg and Bremen and also for a disposal site for industrial waste in Bremen (Hamer, 2005).

However, compared to natural clays and silts high water contents and contaminants hinder the substitution of primary resources by dredged material. Stabilization and immobilization techniques try to improve the characteristics of the dredged material. After dewatering chemicals such as cement, calcium aluminates, fly ashes, benthonite or other clays, phosphates, lime, oil residue and silicate fume are added. The later degradation of organic matter, which is higher in dredged material than in primary silts and clays usually applied for containment layers, can have an influence on the long-term stability of the construction and the chemistry of the pore water. This may have an effect on the emission of nutrients and contaminants.

The substitution of clay by sludges or dredged sediments in order to produce bricks has been conducted in industrial scale (Hamer and Karius, 2002). The brickwork of Hanseaten-Stein Ziegelei GmbH in Hamburg operated with an annual production capacity to approximately 5 million bricks. The bricks were destined predominantly for industrial and commercial buildings as well as for local authority builders. Mainly sediments from the port of Hamburg were used. Additionally, pilot tests were conducted with sediments from the ports of Bremen, Venice and Antwerp (Hamer and Karius, 2002).

Using harbour sediments for brick-making has to comply with regulations considering the national waste-, emission-, construction- and soil protection acts. The German regulations are fulfilled (Hamer and Karius, 2002), however, compared to conventional brick-making energy consumption is higher using harbour sediments instead of natural clays due to the higher water content. An important environmental benefit of this technique is the total destruction of all organic pollution and the final fixation of most potential inorganic contaminants in the product. The whole life cycle of the products had been investigated, including the phases of bricks use: storage, masonry as well as recycling after demolition (Hamer and Karius, 2002).

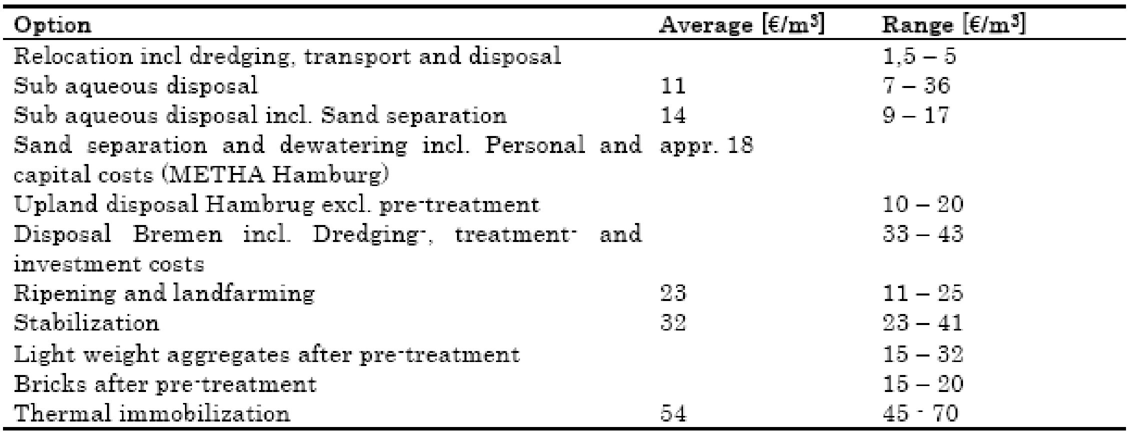
The technology to produce cement from dredged material called Cement-Lock, can treat organic as well as inorganic contaminants at widely varying concentrations and is applicable to a variety of feedstocks (Hamer, 2005). Sludge coming from marble processing could be used as additive material up to waste sludge of 9 % in cement (Arslan et al., 2005). Substitution of textile ETP sludge for cement, up to a maximum of 30%, may be possible in the manufacturing of non-structural building materials (Balasubramanian et al., 2005). During Cement-Lock processing, sediment and other feedstocks are blended with mineral modifiers to achieve the desired elemental composition. Type of cement and the aging time exerted a strong influence on the concretes microstructure and resistance to axial compression (Gemelli et al., 2001). The particle size of the sediment does not affect the process because the mixture of sediment and mineral modifiers is melted to a homogeneous molten phase. The molten stream is cooled and granulated and converted into a product called “Ecomelt”. Ecomelt can be ground and blended with Portland cement to yield construction-grade cement for use in the manufacture of concrete.

Thermal desorption is applied to treat dredged material containing volatile contaminants, e.g. mineral oil, mono aromates, PAH's, PCB's, cyanide, chlorinated solvents and TBT(Hamer, 2005). The operating temperature is dependent on the contaminant as well as the water content of the material. The central treatment unit for thermal desorption is often a rotary drum. The contaminants in the material entering the drum are volatised. The processed and cleaned material is leaving the installation through a discharge system with water nozzles to cool it down and preventing dust formation. The exhaust gas streams leaving the rotary drum have to be treated as well in order to comply with exhaust gas standards. After such a treatment dredged sediments are prepared for reuse in order to substitute primary materials.

Costs of some treatment options from experiences in Germany and The Netherlands are summarized in Table 2.2.3.1. But costs are a mirror image of the boundary conditions like capacity of the facility, duration of the project, amount of sediment to be treated, sediment characteristics and more (Hamer, 2005). The general practice of rarely offering long-term contracts -with some exceptions like the call for tender for a period to 20 years for a large volume in Hamburg or in New York - blocks alternatives, which require high investment costs compared to disposal sites or relocation.

Some important environmental aspects like the reduction of space consumption, protection of climate or re-use of secondary material in order to substitute primary resources are complicated to be evaluated and almost ignored in common cost calculations. Consequently, in their broader view of economy, neglecting environmental effects bears the risk of a loss of capital stocks, consequently decreasing the economy and social welfare on the long term. To reach a sustainable development the value of natural resources must be integrated into economic calculations.

Table 2.2.3.1. Costs of treatment and disposal (€/m^3 in-situ)
(Source: Netzband et al., 2002).



Option	Average [€/m^3]	Range [€/m^3]
Relocation incl dredging, transport and disposal		1,5 – 5
Sub aqueous disposal	11	7 – 36
Sub aqueous disposal incl. Sand separation	14	9 – 17
Sand separation and dewatering incl. Personal and capital costs (METHA Hamburg)	appr. 18	
Upland disposal Hambrug excl. pre-treatment		10 – 20
Disposal Bremen incl. Dredging-, treatment- and investment costs		33 – 43
Ripening and landfarming	23	11 – 25
Stabilization	32	23 – 41
Light weight aggregates after pre-treatment		15 – 32
Bricks after pre-treatment		15 – 20
Thermal immobilization	54	45 - 70

A new time scale is important because long-term-effects have to be considered to build up a sustainable sediment management. Sustainability is the starting point because a sustainable development is a development that ensures that the use of ecological resources and ecosystems today does not damage prospects for their use by future generations. So assessment on the "long-term" should consider the time span of a generation or more, that is minimum 30 years. Methods applied to investigate potential emissions have to consider the whole product's life-cycle (Figure 2.2.3.2) including the phases of storing the product, its use, the potential re-use under different boundary conditions and at last the disposal of the former products as a part of demolition masses.

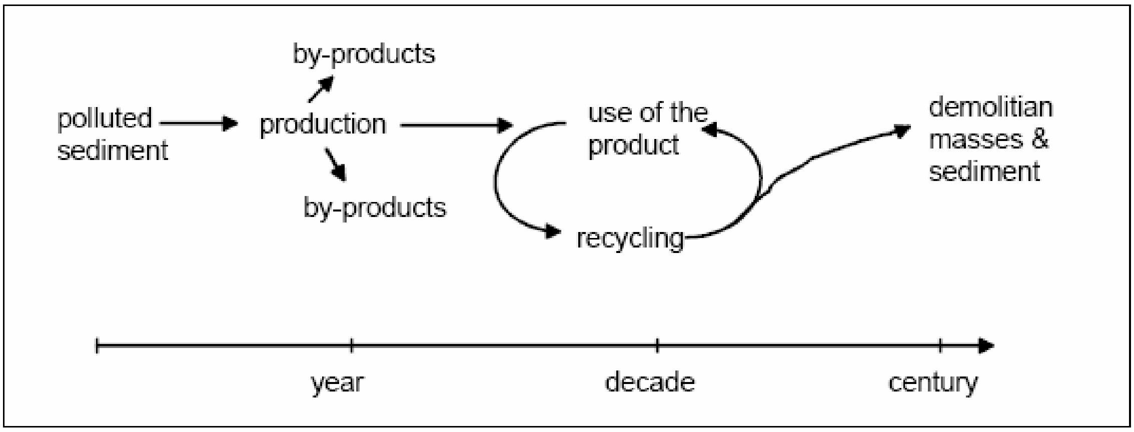


Figure 2.2.3.2. Life-cycle of products
(Source: Hamer, 2005).

Regarding disposal or treatment options this means European standards for assessing treatment and disposal alternatives should consider the present know-how about long-term effects (e.g. the life-cycle of sediments and products and effects on mobility and bioavailability of pollutants with time).

During the use of products the physical and geochemical circumstances can change in a way that former stabilized pollutants can be mobilized again. A decrease of grain sizes due to demolition of construction material like light weight aggregates will increase the effective surfaces of products. So leaching can be more effective than before. Additionally the pH-value of the solutions leaching from the products can change due to acid rain or mixing with alkaline components like mortar or cement or a change in the redox conditions. Changes like that can influence the mobilization dramatically, so that any re-use of materials containing pollutants bears uncertainties as long as changes of physical and chemical circumstances are neglected.

CHAPTER 3

CERAMIC TILE

Ceramic tiles and their historical background, Ceramic tile sectors in Turkey and its position in the world and Ceramic tile processing will be explained in this chapter of the thesis.

3.1. Ceramic Tiles and Their Historical Background

The history of tiles dates back as far as the fourth millenium BC where in Egypt tiles were used to decorate various houses. In those days, clay bricks were dried beneath the sun or baked, and the first glazes were blue in color and were made from copper.

As early as 4,000 BC ceramics were also found in Mesopotamia. These ceramics bore decorations which were white and blue striped and later possessed more varied patterns and colors.

In China, the great center of ceramic art, a fine, white stoneware with the earliest Chinese glaze was produced during the Shang-Yin Dynasty (1523-1028 BC).

Through the centuries, tile decoration was improved upon as were methods of tile manufacture. For example, during the Islamic period, all methods of tile decoration were brought to perfection in Persia. Throughout the known world, in various countries and cities, ceramic tile production and decoration reached great heights. The tile mosaics of Spain and Portugal, the floor tiles of Rennaisance Italy, the faiences of Antwerp, the development of tile iconography in the Netherlands, and the ceramic tiles of Germany are all prominent landmarks in the history of ceramic tile (WEB_1 2006).

In the early days, the tiles were hand-made - that is to say - each tile was hand-formed and hand-painted, thus each was a work of art in its own right. Ceramic tile was used almost everywhere - on walls, floors, ceilings, fireplaces, in murals, and as an exterior cladding on buildings.

Today ceramic tile in the United States as it is throughout the world is not "hand-made" or "hand-painted" for the most part. Automated manufacturing techniques are used and the human hand does not enter into the picture until it is time to install the tile.

As in the early days, ceramic tile is still used indoors as well as outdoors. It can be found on floors, walls, counters, fireplaces, fountains, exterior building walls, etc.

3.2. Ceramic Tile Sectors in Turkey

The ceramic production tradition that started 8.000 years ago on Anatolian soil, was carried to the industrial dimension starting from the second half of the 20th century and the Turkish ceramic tile sector has succeeded especially by the investments it made after 1990. Today Turkey is one of the leading countries in ceramic tile production all around the world.

With its production over 180 million m^2, Turkey is the 5th leading ceramic tile producer in the world and 3rd largest in Europe. Ceramic tile production of Turkey constitutes 3.5% of world production and 11% of European production. Turkey is the 8th largest market in the world regarding the ceramic tile consumption. 99% of annual domestic demand of 110 million m^2 is satisfied by domestic production.

The total capacity of the sector with 24 companies carrying out production was 250 million m^2 in 2001. Kale, Toprak, Ege and Eczacıbaşı Groups, which are the leading companies of the sector in Turkey, are also among the largest manufacturers in the world. Kale Group has the world's largest factory carrying out integrated manufacturing under a single roof with its capacity of 60 million m^2.

Turkish ceramic tile producers are technologically superior to their competitors as most Turkish companies started production after 1990 and existing firms are continuously renewing their technological investments. The production capacities of many Turkish companies, which are around 10 million m^2, are much greater than those of their foreign competitors (WEB_2, 2005).

As the Turkish ceramic raw material reserves are large enough to satisfy sector's demand and as they are of world standard quality, Turkish companies have installed their own raw material preparation facilities within their organizations. Turkey is satisfying almost its entire raw material requirement through domestic production. Turkish ceramic companies, adopting a complete and full service concept, support their customers with their own foreign trade organizations abroad with the emphasis they place on skilled manpower and with a view to bring their post production services beside the manufacturing process to the highest level.

Turkish companies export their products to 70 countries today and are able to compete easily with their rivals not only in respect of quantity but also where design and product diversity are concerned as well. The performance displayed by the sector in recent years, is the most significant proof of this phenomenon. In the period between the years 1990-2000, the exports of the sector have increased 8 fold. Turkey is the 3rd largest exporting country in the world with its exports of 60 million m^2.

The expansion of the Turkish ceramic tile sector in international markets is in progress, relying on the thrust it gets from all its past accumulation and at a great speed. The number of overseas markets of Turkish ceramic companies, which participate in exhibitions of Cersaie in Italy, Cevisima in Spain, Coverings in USA, Mosbuild in Russia, Bau in Germany; is increasing each year and their international area of influence is getting wider. Turkey brings together the largest ceramic manufacturers in the region with their customers in the world markets, at the UNICERA International Ceramic and Bathroom Products Exhibition organized each year in Istanbul/ Turkey.

Turkey is advancing rapidly in an effort to be the leading exporting country in the world every other year, by increasing its market share in countries that it exports to and with successes it has achieved by building permanent relationships with new markets.

3.3. Ceramic Tile Processing

The desired color for a wall tile body, in most parts of the world, is white or buff. Some producers manufacture a pink or red body, depending on the availability of local materials. The iron content of the clays and/or other minerals used in tile manufacture is generally the determining factor in the tile body color. The higher the iron content, the redder the body. Kaolinite, illite, smectite, talc, pyrophyllite, feldspathic minerals, carbonates, silica sand are well known raw materials for tile production.Combinations of these materials are therefore used by the ceramist to control the final desired properties of the ceramic body during manufacture.

A description of the basic processing and equipment used in ceramic tile manufacture is included below to familiarize the non-ceramist with the basics of this technology. With few exceptions, the equipment and processes used in dry pressing and/or extrusion of ceramic tile are similar to those used in all parts of the ceramic industry and will not be repeated for other areas.

Wall tile includes that family of glazed tile which exhibit relatively low mechanical strength and high water absorption. The process of manufacturing wall tiles may include tunnel kiln firing (14 hour cycle) or fast fire roller hearth kilns (40 to 60 minute cycle). The more modern roller kilns are replacing the older tunnel kilns throughout the world as the standard firing vehicle for all types of ceramic tile. Figure 3.3.1. illustrates a typical process flow diagram for the production of wall tile, exhibiting the "two-fire" process commonly used in today's wall tile industry.

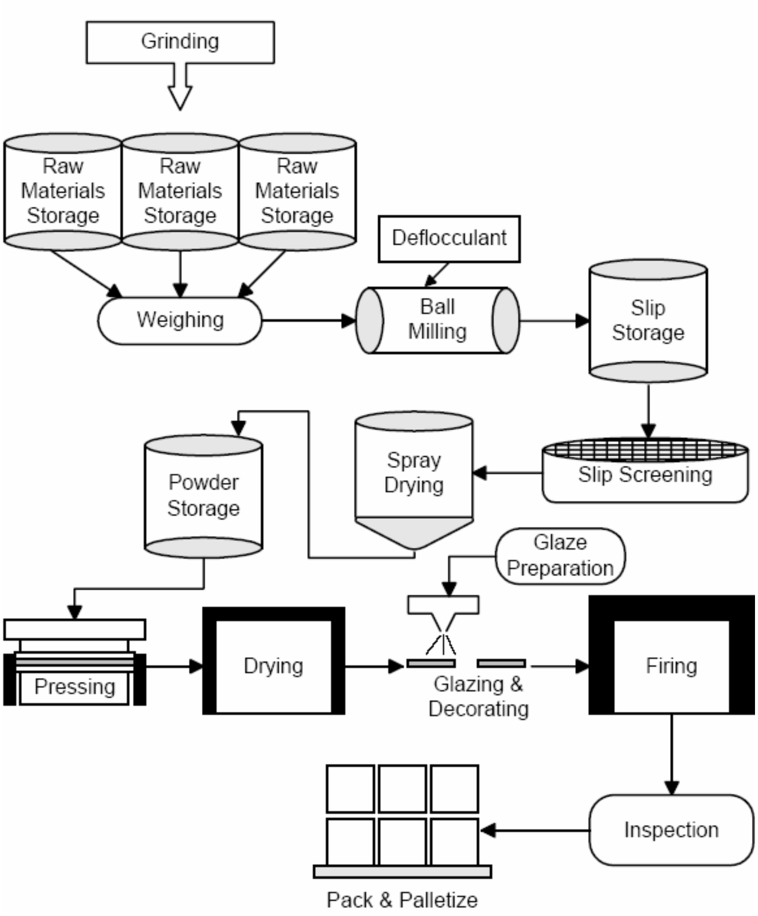


Figure 3.3.1. Process Flow: One-Fire Floor Tile.

Floor tiles have higher mechanical strength and lower water absorption, reflecting the tougher use criteria to which floor tiles are exposed. In today's state-of -the-art technology, floor tile are usually produced by the once-fired process as seen in Figure 3.3.1.

3.4. Materials Preparation

Hard raw materials, such as calcium carbonate rock or feldspars, are reduced to desired size by successively grinding through one or more jaw crushers and then to a ring mill for final sizing. Oversize particles are screened after ring milling and returned back through the process in a closed loop system.

Most clay materials are not beneficiated at the plant site prior to blending or milling, but in some cases, especially where continuous ball milling is subsequently used, the clay portion of the body may be pre blended in high speed blungers to insure dispersion or “slaking” of the clay particles prior to final blending or milling.

Weighed materials are fed to a collector belt which transfers the composite to a large ball mill. Water is automatically fed to the mill through a metering system also controlled by the computer. This portion of the process is by far the most crucial, since the old saying of “garbage in, garbage out” is never more true than in the correct weighing and /or proportioning of raw materials in the first step of a ceramic process. The control of all raw materials in the process is extremely important for continuous, smooth running of a plant.

Milling of clay slurries is in ceramic- or rubber-lined ball mills with capacities from 1000 to 3000 kilograms. The grinding media are silica pebbles from 20 mm to 60 mm in diameter. Silica pebbles are generally used, especially in rubber-lined mills, since the alternative alumina pebbles are more prone to promote excessive wear on the rubber lining. The intimate mixing of the raw materials is extremely important to the uniform completion of the solid state reactions which take place during firing.

The size distribution of the pebbles is important to promote grinding; a usual distribution being: 45-50% pebbles from 20-30 mm diameter, 25-30% pebbles from 40-50 mm diameter and 20-25% pebbles from 50-60 mm diameter. As the pebbles wear with continued use, the normal practice is to add pebbles of the largest size to replenish the charge, since the wear of the media will fill in the voids of the charge in the mill. Grinding speeds may be increased with the use of alumina pebbles, but the increased speed must be weighed against the increased cost of the alumina media. The theory of milling speeds versus mill charge versus media composition versus materials charge can take up many pages of specific description. The important control parameters for the milling process are media charge and size distribution, raw material charge, mill rotation speed, type and amount of deflocculant, water content.

The process of defloculation involves the use of one or more agents whose purpose is to impart a charge to the surface of the clay particles, thereby allowing those particles to repel each other in the slurry, allowing less water (which must subsequently be removed by spray drying or some other process) in the slurry and reducing the viscosity of the slurry to facilitate pumping. Common deflocculating agents used in the ceramics industry include: trisodium phosphate, sodium silicate, and sodiumhexametaphosphate.

The total milling time for the slurry (or slip) is usually governed by the percentage of residue in the slurry which will not pass through a sieve of some known dimension. A representative residue content would be 8 to 9% on a 100 mesh sieve. Generally, this would be the result obtained by milling a typical tile formula of 1700 kg. total weight for 8 hours. After milling, the slip is stored for up to 24 hours, generally in underground storage tanks, to allow mixing with slip from other mills and to allow the formula to come to equilibrium.

The most common method today of preparing the powdered body material for the forming process is spray drying. A spray dryer is a large, cylindrical, vertically oriented chamber into which the slurry is pumped under pressure through nozzles of controlled orifice size. Heated air (500 to $600^{O}C$) is forced upward into the chamber. Since the natural state of least free energy of the droplets of slip is a sphere, the resultant product of the spray dryer is spherical powder particles of controlled, generally uniform, grain size, with 5-6% residual moisture, ready (after an aging step) for pressing. This aging step, usually twenty four hours, is necessary to allow the residual moisture in the particles to equilibrate, since the outside of the particle is dryer than the inside immediately after spray drying.

Tile shapes are pressed on hydraulic presses, ranging from 500 to 2500 tons of capacity, using steel- or rubber-lined steel dies. Spray dried powder lends itself ideally to hydraulic, rapid, automatic pressing. The characteristic free flowing nature and uniform particle size of these powders are ideal for rapid, uniform filling of die cavities, even for somewhat complex trim shapes.

The 5-6% residual moisture in the pressed piece must be removed prior to firing of the tile to prevent the tile from exploding due to a sudden formation of steam inside a sealed surface. Dryers are either vertical or horizontal depending on floor space available, although horizontal radiant dryers are being used more frequently because they require less handling of the “green” tile and result in less breakage and/or chipping of the tile prior to glazing or firing.

Firing is the main step in any ceramic process. Firing is characterized by a number of complex physical changes and chemical reactions which determine the final characteristics of the finished tile product.

Up to 100°C, the elimination of hygroscopic water takes place. This moisture may be present due to incomplete drying prior to glazing, or as a result of moisture reabsorbed during the glazing process. Up to 200°C, the zeolitic water, molecular water bound to the crystalline lattice by absorption, is eliminated. From 350 to 650 °C, the combustion of organic substances usually present in clays occurs. This is followed by the dissociation of sulfides and sulfates with the resultant emission of sulfurous acid. Combined water, with the resultant alteration of crystal lattices, is expelled from 450 to 650 °C. At 573 °C, the transformation of alpha to beta quartz occurs with an abrupt increase in volume. CO_2 is volatilized between 800 and 950 °C due to the decomposition of lime and dolomite. Beginning at 700 °C, new crystalline phases begin to form. These phases consist of silicates and complex aluminosilicates. These phases form the final crystalline structure of the tile. Glass phases holding the crystalline matrix together begin to form from 1000 up to 1200 °C depending on the body formulation. Glaze melting begins in this region as well.

Two basic types of kilns remain in service today with the older tunnel kilns being gradually replaced or outnumbered by roller hearth rapid fire kilns (Figure 3.4.1.). Firing in tunnel kilns is done on refractory setters, either manually or automatically loaded. Tunnel kilns remain in wide use today for smaller tile sizes such as 26 x 26 cm. Roller hearth kilns fire the tile on ceramic rollers, almost always automatically loaded.

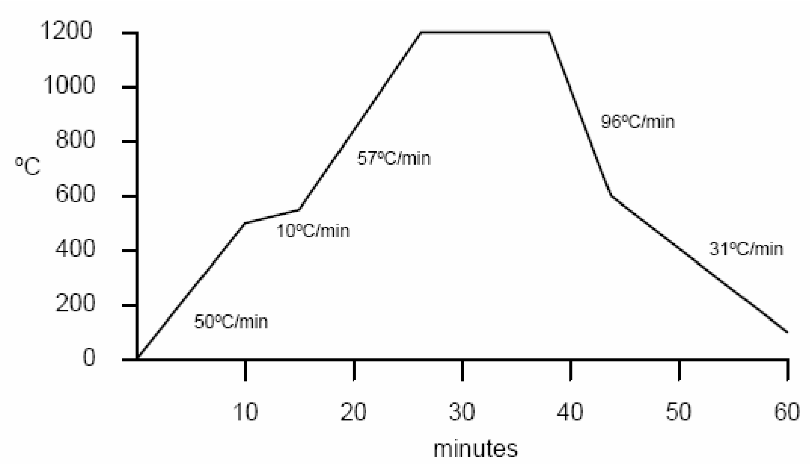


Figure 3.4.1. Typical Fast Fire Curve for Roller Hearth Kiln.

3.5. The Use of Marine and Other Sludge in Ceramic Industry

Although there is limited literature on ceramic tile production by using marine sludge mixing with ceramic tile raw materials, a lot of literature can be found connected to the production of bricks than any other ceramic product by using variety of sludge such as sewage, galvanic, granite, textile etc.

A review of the literature on the use of sewage sludge shows that it could be used as an additive compound in ceramic building materials (Alleman, 2003). Actual production levels involve the consumption of huge amounts of mineral resources, and the heterogeneous character of natural raw materials, the use of several formulations and, not less important, the firing process might ensure the desired inertness of final waste-containing products with respect to the ceramic matrix (Ribeiro et al., 2002). The increase of water absorption with the increase of the sludge percentage is clear, giving rise to a linear relation. On the other hand, the addition of sludge gives rise to a decrease of the bending strength, in such a way that the selection of the adequate percentage of sludge to be added to the body can be controlled by standards applied to specific construction materials (Jordan et al., 2005).

The study indicated that there is the possibility of combined utilization of sludge from the Sofia wastewater treatment plant and waste products from coke-chemical production as additives to brick clay (Balganova et al., 2003). The green flexural strength decreases with the fly ash content increase because of a non-plastic material. Batches with limestone promote, as desired, an appreciable reduction in the total linear shrinkage. This fact is responsible for the flexural strength decrease and for the water absorption increase. When feldspar was added in ceramic batches containing fly ash and clay, there was a porosity closing and then flexural strength increase. (Zimmer and Bergmann, 2006).

The ash resulting from the burning of cellulignin, a biofuel produced by acidic prehydrolysis of any cellulose-containing biomass, can be incorporated into vitrified ceramics as a technologically advantageous and environmentally correct solution. The ash presents partially nanometric particle size and forms agglomerates with coarse pores that can be associated with the porosity found in the incorporated ceramic body. During firing the ash acts as a flux and contributes to the consolidation of the ceramic structure. This promotes a reduction in water absorption and an increase in mechanical strength. Leaching tests showed that potentially toxic metals present in the ash become inert after the ceramic firing (Pinatti et al., 2006).

The regression models can be used to select the best combination of those three raw materials (clay mixture, potash feldspar and quartz) to produce a ceramic body with specified properties such as linear firing shrinkage and water absorption (Correia et al 2004). Granite sawing wastes, produced by the granite processing industry, as alternative ceramic raw materials for production of bricks and tiles, yielded the following conclusions. The addition of wastes in ceramic compositions for production of bricks, up to 35% in weight, an increase in the modulus of rupture was observed, ceramic compositions with additions of wastes can be used to produce wall and floor tiles, and by firing at 1200 °C they can be used to produce ceramics with water absorption lower than 3% (Menezes et al., 2005). The incorporation of high levels (up to 50 wt %) of residue in brick-type (BT) or floor tile-type (FTT) formulations is possible (Ferreira et al., 2002). Suitable incorporation of granite sludge can result in porcelain tiles with superior properties, in terms of water absorption (0.07%) and bending strength (>50 MPa). Sludge incorporation had negligible effect on density, shrinkage and plasticity during all stages of tile-production process, anticipating no modifications in the industrial production line (Torres et al., 2004).

In order to make ceramic tile with mixing granulated blast furnace slag, optimum compositions were found to be where calcia-silica ratio were in the range of 0.1–0.3 where mechanical strength and water absorption of the fired specimen were in the range of 28–38 MPa and 2.5–0.1%, respectively. The increase in mechanical strength of the sintered specimen with increasing amount of the slag up to 50% was due to the formation of large number of smaller grains embedded in the glassy matrix. Use of higher amount of slag beyond the optimum composition range was found to be counter productive due to insufficient liquid formation at the sintering temperature (Ghosh et al., 2002).

Samples were prepared by mixing clay soil with different quantities of the tannery sludge up to 40 wt%, and after drying, the samples were annealed at 950, 1000 and 1050 °C. The bricks obtained showed qualities comparable to those obtained in South Africa. The results show that the compression strength of the brick decreases with the sludge ratio in the clay, but improves with an increase in the kiln's temperature (Werther and Ogada, 1999). The raw materials, tannery sludge and clay, were mixed together in different proportions. The main sludge contaminant i.e. chromium, could be immobilized within a finished ceramic product. The properties of the ceramic materials produced are acceptable for applications such as bricks for the building industry (Basegio 2002).

The bricks produced with spent grains possessed a comparable or higher strength, a higher porosity and a reduced density after firing than those from standard production clay. Because of the lower sintering temperatures the fired clay product was more strongly sintered, exhibiting both greater strength and higher porosity (Russ et al., 2005). The maximum percentages of dried sludge and sludge ash that could be mixed with clay for brick making are 40% and 50% by weight respectively (Tay et al., 1999).

It was reported to be able to produced a brick which has `less firing shrinkage`, `less weight loss on ignition` and `gaining more compressive strength` by using sludge (20 to 40%) with 13 to 15% optimum moistures and fired at 1000 ºC (Lin et al., 2001). Bricks manufactured from dried sludge collected from an industrial wastewater treatment plant were investigated and obtained the result of that proportion of sludge in brick is 10%, with 24% optimum moisture content, prepared in the molded mixtures and fired between 880 °C and 960 °C (Weng et. al., 2003). Hydroxide-metal sludges from electroplating industry are a potential source of environmental contamination due to their high content of heavy metals. The incorporation of these residues in a ceramic matrix can be a promising way to suppress the harmful effect of metals normally present in those sludges (Magalhaes et al., 2004).

The sediment is regarded as a suitable raw material for brick production because of its perpetual availability, homogeneity and mineralogical, petrographic and chemical composition (Hamer et al., 2002). A brick made of harbour sediments 50% wt. from the port of Bremen-City was characterized. The leachability of the sediment brick shows high values only in the acidic range. The result is that the sediment brick has no hazardous potential exceeding that of other bricks (Hamer et al., 2001). Giese et. al. reported that the brick which contains 50% marine sludge by weight presents usable properties (Giese et al., 2003).

Dredging spoils deriving from the Venice lagoon were vitrified with the addition of 20% of glass cullet that ensured the production of an inert glass. This sediment is classified as toxic waste because contains several heavy metal ions and organic pollutants and was successfully vitrified at 1200–1350 °C. The process consists in a viscous phase sintering of pressed glass powders which are transformed in glass ceramic during the densification process. Mechanical properties of the final glass ceramic material in the range of traditional construction materials suggest its utilization for application in the building industry (Benstein et al., 2002).

Fabricating sintered glass-ceramics from vitrified urban incineration waste that was not capable of bulk crystallization could be possible (Romero et al., 2001). A mixture of up to 30% fine waste-brick additives can be used in brick production and economically fired at 900 °C. Compressive strength values increase with increasing sintering temperature. Increase in the waste brick content leads to decreased durability and compressive strength meets the required speciation (Demir et al., 2003).

The ceramic materials produced using powders obtained from calcined dredging spoils alone (DS), or in mixture with municipal sewage sludge (MSS), bottom ash (BA) or steelwork slag (SS) are able to immobilize most of the hazardous elements contained in the starting materials (Baruzzo et al., 2006). The mechanical properties of the materials obtained by sintering DS alone or mixtures DS +MSS and DS +BA are good, due to the formation of monolithic materials having fine grains embedded into a vitreous phase and a low residual porosity; those of the composition MS+ SS are low since fired materials containing large defects. DS and DS +BA materials have also a light colour and could be used to prepare value added products. On the other hand, the same cannot be excluded for the powders obtained from incinerated DS, MSS and BA since the relative fired materials have fair mechanical properties and the release of hazardous elements is low.

The shrinkage on firing is high for all the materials produced in the present work and further formulations are necessary before undergoing an eventual industrial production. 30% by volume of sludge is blended with clay for the production of stock bricks (commons), and between 5 and 8% for face bricks. The organic matter in the sludge begins to burn causing a rapid increase in the bricks' temperature to 800 °C. At the point along the kiln where the sludge has completely burnt and the temperature gradient decreases, an external fuel is burnt to raise the temperature to 960 °C. The appearance of the bricks made from clay mixed with sludge is reported to be excellent, being uniform in colour and texture, and free from extensive cracks. They are indistinguishable in both appearance and odour from conventional bricks. Average compressive strength was 40.7 and 38.3 MPa, for face brick and stock bricks, respectively (Werther and Ogada, 1999).

Leaching Test apply to determine ability of keeping heavy metal in ceramic structure. For most metals, leaching rate follows a zero-order kinetic law, with values between 0.001 to 0.1 mg/(g day cm^2). Leaching velocity tends to increase with rising atomic numbers: Zn <Cu <Ni <Cr. These values depend exponentially on the relative sludge content (Magahaes et al., 2005). The dominant mechanism of the inertization process and the relevant influent parameters are not clearly known, mostly due to the complexity of the systems. To define the relevance of each experimental variable on the inertization process of the used galvanic sludge it can be done a statistical study in addition to experimental study. The relative amount of sludge in the mixture, the calcination temperature and the agglomeration state of the sample were found to be the most influent parameters of the inertization process. The incipient reaction between sludge and ceramic matrix components points out for the dominance of a macro-encapsulation mechanism (Magallhaes et al., 2004b).

Increasing ignition loss of a compact specimen may increase the porosity and decrease the densification effect after sintering. Increasing the sintering temperature to 1120 °C, causes both a decreasing swelling rate due to only a slight change in crystalline phase and a decreasing porosity. However, elevating the sintering temperature again to 1140 °C, causes the densification to become more increasingly significant, leading to a total shrinkage in volume. Sintering at a high temperature enhances the densification, closes some of the open pores, and causes moisture absorption rate to decrease. The absorption also decreases with increasing sintering time and compact pressure. In addition, decreasing the absorption implies a decrease in open pores and an increase in compressive strength. The morphology analysis reveals a decreased average diameter in the pores, due to filling by smaller particles when the sintering temperature is elevated.

The concentration of TCLP leachate for Pb, Cd, and Cr denotes a decreasing leaching tendency with increasing sintering time. However, specimens at different sintering temperatures reflect that the leaching behaviors depend primarily on the types of heavy metals and/or their compounds formed at that temperature. The specimens sintered at 1100 °C exhibit a compressive strength ranging from 60–80 kg/cm^2, while those sintered at 1140 °C enhance the strength to 120 kg/cm^2. The maximum strength developed at 1140 °C, and 280 kgf/cm, 4000 psi for 60 min is 230 kgrcm^2 (Wang et al., 1998).

There is an interesting study that dewaterability, heavy metal release and reuse characteristics and reuse of Golden Horn surface sediment were investigated under remediation considerations. Determination of factors was like cost effective volume reduction process. Twenty five percent and seventy five percent of the water content were of free and immobilized, and of bound nature, respectively, with a high resistance value revealing poor dewaterability characteristics. The leachate did not contain toxic heavy metals, even at pH 3. The sediment had strong absorbability for Cu and Pb, and high buffering capacity. The reuse of the dried sediment as a clay mixture in brick manufacturing seemed possible up to 40 percent (Karpuzcu et al., 1996).

Common sea shells are composed by layers of $CaCO_3$, sandwiched between biopolymers. This structure provides strength, hardness and toughness (e.g. nacre is 3000 times as tough as its constituent phases) (Neves et al., 2005). Effect of carbonate and salt additives were explained a study (Cultrone et al., 2005). The behavioural differences between specimens with and without carbonates can be explained by the different evolution of texture and mineralogical composition developed during the firing process. Carbonates are shown to result in bricks with different mineralogy, depending on firing, but with a stable microstructure within a wide range of temperatures. The carbonates in the raw clay promote the formation of fissures and of pores under 1 mm in size when the bricks are fired between 800 and 1000 °C (Cultrone et al., 2004). This may be an advantage when manufacturing pottery but these pieces lack mechanical resistance to high temperatures. Salt partially modifies the mineralogy of the bricks, acting as a melting agent, especially at high firing temperatures, and giving rise to more resistant products which are suitable for restoration work (Cultrone et al., 2005).

An important aspect during thermal processing of sewage sludge is its combustion mechanisms. One important issue of sludge combustion is the emissions of pollutants gases as well as the handling of solid by-products. Of concern include the heavy metals, mercury, dioxins and furans, acid gases, as well as NO_x and N_2O (Werher and Ogada, 1999).Chlorine, fluorine emissions are actually important in ceramic industry. The emission factors are F initial content, temperature of firing and calcite content. Chloride emissions are higher at 1000 °C due to its association with illite, but quantities remain low. The initial content of F was reduced with the proposed mixing scheme and the emission is not important if the firing temperature is 850–900 °C. If the products require a firing temperature >950 °C, it is better to avoid use of the red loam in percentage >30%, because its higher F initial content and its lower proportion of carbonates produces higher emissions. The elimination of red loam could produce problems of color and mechanical shrinkage. The addition of rich aluminum clays could improve the mechanical shrinkage and the red color could be obtained controlling the oxidant atmosphere of kiln (Gonzalez et al., 2002).

The optimum firing temperature ranges under laboratory conditions were from 1120 to 1140 °C (wall) and 1180 to 1200 °C (floor). Increased presence of magnesite, as a co-fluxing material, in the multipurpose body seems to accelerate the vitrification process. Fired samples indicated the presence of anorthite as newly formed and quartz and albite as residual crystalline phases, plus a small amount of mullite and glassy phase. The anorthite and mullite were observed to be tri-dimensionally dispersed in a silico-aluminate matrix. Regarding possible single fast firing difficulties of $CaCO_3$ presence due to its decomposition in a wide temperature range, it was an alternative calcium-containing raw materials that do not emit gas during firing, such as wollastonite (Kara et al., 2006). The firing of a mixture of specific percentages of three components (clays, sludges and forest debris) resulted in a lighter and more thermal and acoustic insulating brick, compared with conventional clay-bricks. Volatile organic compounds (VOC) emission from the manufacturing of ceramics is the most important aspect to control. Drying of raw sewage-sludge and firing processes were considered separately (Cusido et al., 2003).

As pollution prevention and cleaner production are important elements of industrial ecology, the different definitions and approaches of industrial ecology as a term also need clarity. It was applied in an industrial ecosystem project (INES) in the Rotterdam harbour area. Feasibility studies showed the potency to reduce the use of energy, water and bio sludge significantly (Baas, 1998).

Interesting results could be encountered when sewage sludge were sintered. Sintering produces potentially useful ceramic materials with maximum densities resulting from firing between 1000 and 1020 °C. Density decreases as the firing temperature is further increased, due to a bloating effect associated with the formation of high volumes of approximately spherical pores. The major crystalline phases present in both as-received and sintered sewage sludge ash (SSA) ceramics are quartz, the calcium magnesium phosphate mineral, whitlockite and hematite. The as-received and sintered SSAs have low acid neutralisation capacities and leach significant fractions of Cu, Mn and Zn under acid conditions. Sintering SSA was found to reduce metal leaching for all metals (Cheeseman et al., 2003).

The sludge ash consists of SiO_2, Al_2O_3, Fe_2O_3, and P_2O_5 as the major components. The water absorption rate of the sintered sewage sludge ash samples decreased when the firing temperature was increased from 800 to 900°C. When the heating temperature reached 1000 °C, the absorption rate decreased significantly. The bulk density of the sewage sludge ash samples increased by 2.3 g/cm^3 when the heating temperature was increased from 900 to 1000 °C, indicating that the densification was affected by heating. The porosity of the sintered sewage sludge ash samples ranged from 36% to 39% when the heating temperature ranged from 600 to 900 °C. The least porosity occurred at 1000 °C; the sintered samples were well densified. When the temperature was between 900 and 1000 °C, the strength appeared to increase significantly, reaching 2040 kgf/cm^2, implying an advance in densification due to sintering (Lin et al., 2005).

3.6. Characterization of Ceramics

Some calculations can be used for characterization of samples (Jones and Berard, 1993). One of them was done for loss on ignition (LOI) calculation. When a raw material is heated in air, it often loses weight as a result of volatiles being driven off. In general, any material whose oxide formula contains H_2O, CO_2, SO_2, or NO_2 units will lose weight if heated to a sufficiently high temperature. Chemically combined H_2O, CO_2, SO_2, and NO_2 come off irreversibly at specific temperatures for each material. On the other hand, water of hydration (molecular water such as that in the mineral borax) is lost gradually with heating. Any carbonaceous material present combines with oxygen from the air to form volatile oxides which also leads to weight loss.

The amount of weight lost by a material during heating is an important characteristic of the material. This weight loss, called the loss on ignition (LOI), is readily determined by experiment or may be calculated for a material if its exact oxide formula is known. A small representative sample is first dried to constant weight W_D at 110 °C and then ignited or heated until it reaches constant weight W_I at a specific temperature. The LOI is then computed as

$$\%LOI = \frac{W_D - W_I}{W_D} \times 100 \tag{3.6.1}$$

The procedure of igniting or heating a ceramic material to drive out volatiles is also called calcination. A material loses some weight during the drying step, which procedes calcination. The amount of this drying weight loss depends on current weather conditions (especially humidity) and the previous method of storage of the material. The drying loss is not included in the %LOI, but it must be known to determine the weight of undried material necessary to give a certain weight of dry material called for in a recipe (or batch formulation). This moisture content can be expressed on either the undried or the dried basis, and it is necessary to specify the basis when moisture content is being reported. On wet basis

$$\%LOI = \frac{W_u - W_D}{W_u} \times 100 \tag{3.6.2}$$

where W_u is the wet (stored or as-received) weight. On the dried basis

$$\%LOI = \frac{W_u - W_D}{W_D} \times 100 \tag{3.6.3}$$

As formed, green raw material which use for producing ceramic material such as tile, white ware etc. contains between 25 and 50 percentage of volume porosity. The amount depends on the particle size, particle-size distribution, and forming method. During the firing process this porosity nearly removed; the volume firing shrinkage is equal to the pore volume eliminated. This firing shrinkage can be substantially decreased by addition of nonshrinking material to the mix: fire-clay brick is commonly manufactured with grog (prefired clay) additions which serve to decrease firing shrinkage. Similarly, this is one of the flint in the porcelain body; it provides a nonshrinking structure which reduces the shrinkage during firing. Terra-cotta compositions composed of mixtures of fired grog and clay, can be made in large shapes because a large part of the raw material has been prefired and the firing shrinkage is low.

If firing is carried to complete densification, the fractional porosity originally present is equal to the shrinkage taking place during firing. This commonly amounts to as much as 35% volume shrinkage or 12 to 15% linear shrinkage and causes difficulty in maintaining close tolerances (Kingery, 1976). However, the main difficulties are warping or distortion caused by different amounts of firing shrinkage at different parts of the ware. Nonuniform shrinking can sometimes even cause cracks to open.

Some confusion can arise in reporting shrinkages unless meticulous care is taken to also report the basis on which the calculation has been made. Thus, if L_f is an as-formed dimension and L_d is the same dimension of the dried unfired piece, the percent volume firing shrinkage is given by

$$\%VFS = \frac{V_d - V_F}{V_d} \times 100 \qquad (3.6.4)$$

The simplest way to determine linear shrinkage is to make a measurement of the dimensions before and after the shrinkage occurs. Sometimes it is not convenient to make length measurements, but displacement volumes for the object can readily be determined (Jones and Berard, 1993). Very simple geometric relationships exist between volume shrinkage and linear shrinkages. For firing shrinkage,

$$\%LFS = \left[1 - \left(1 - \frac{\%VFS}{100}\right)^{\frac{1}{3}}\right] \times 100 \qquad (3.6.5)$$

CHAPTER 4

EXPERIMENTAL

The origin of the raw materials, which were İzmir Bay marine sludge and ceramic tile masse, the pre-treatment of the marine sludge, preparation of the ceramic tile powder mixtures, forming and heat treatment procedures are described in the first part of this chapter. The characterization methods applied on the sludge and tile products by X-Ray Diffraction, microstructure analysis by SEM, TGA analysis, FTIR, ICP-MS, water adsorption, density measurement, elemental analysis (CHNS determination), and leaching tests are explained along with the determination of the mechanical properties and statistical experimental design in the remaining part of the chapter.

4.1. The Raw Materials

In this thesis, treated marine sludge and ceramic tile powders, which is called masse, was used as raw materials. Some treatments that will be mentioned below were conducted on the sludge for the removal of the shells and the salt in order to obtain a suitable material for tile production. The other raw material which is called masse was obtained from Kalemaden Industrial Raw Material Industry Trade Company. Average chemical analysis of the masse is given in Table 4.1.1.

Table 4.1.1. The average chemical analysis of the masse
(Source: Kalemaden Ürün Katoloğu).

Composition	**W %**
SiO_2	67,26
Al_2O_3	19,55
TiO_2	0,71
Fe_2O_3	1,64
CaO	0,56
MgO	0,40
Na_2O	2,18
K_2O	3,41
Loss on ignition	4,17

The masse mainly consists of silica and alumina as given in Table 4.1.1. Sodium oxide and potassium oxide, most probably originating from the added feldspar, exist as fluxing oxides. Other oxides are present in low levels in the masse.

Marine sludge was collected from inner İzmir Bay given in Figure 4.1.1. in January 2004. Some pre-treatment studies must have been done on the sludge because the sludge contains significant amount of salt and shells which could be dangerous for ceramic tile structure. The process explained in Figure 4.1.2 was considered to be satisfactory for the prevention of the damage of salt and shells.

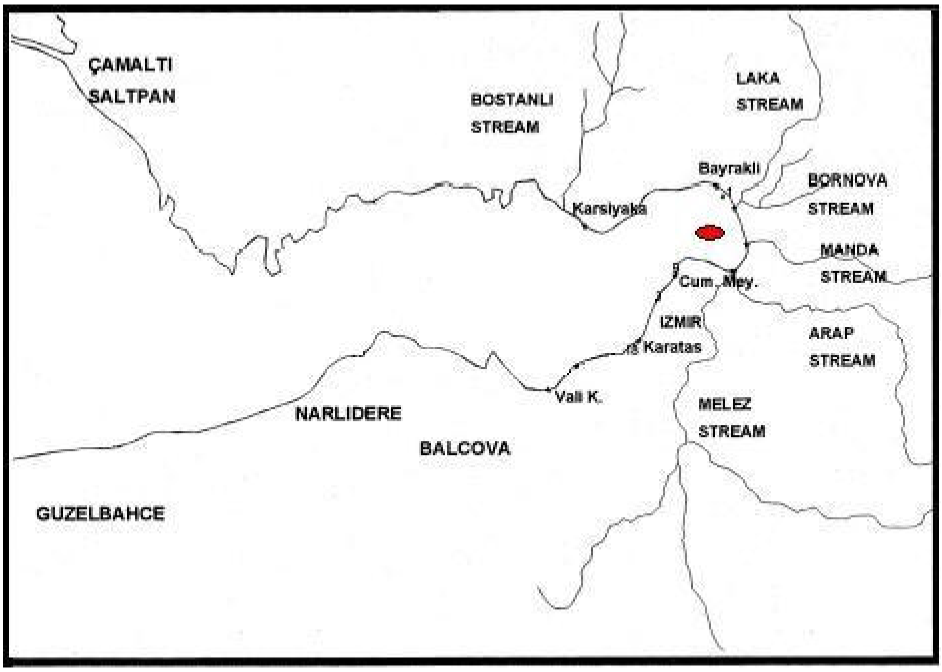


Figure 4.1.1. The map showing sampling region from Izmir Bay.

The sludge was first sieved to remove shells that may potentially deteriorate the ceramic tile structure. The shell-free marine sludge was further mixed with water and soaked in a bin for a day in order to remove most of the salt present which may further cause excessive vitrification during heat treatment. This washing treatment was repeated for three times. The washed sludge was dried in open atmosphere for three days in order to remove disturbing odors and excess water. The air-dried sludge was further dried in an oven at 120 ºC for sixteen hours. Dried sludge was crushed by jaw crusher due to the formation of large marine sludge chunks during oven drying and was further ground by using a disc mill. This grinding step resulted in the relatively faster formation of a marine sludge powder. Flow chart of this process is given below:

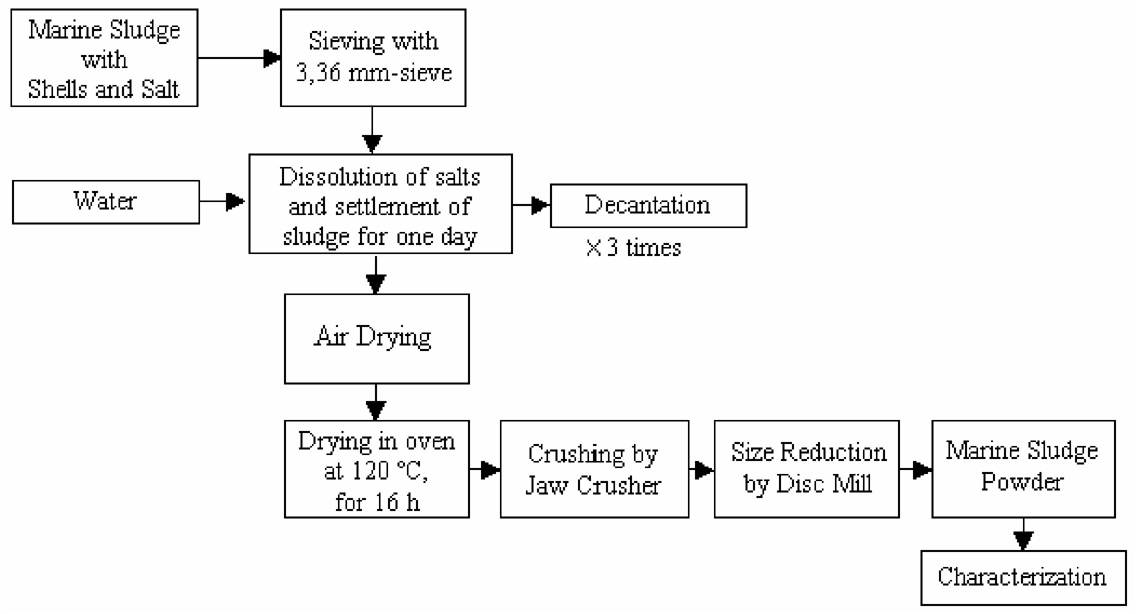


Figure 4.1.2. Flow chat of marine sludge treatment process.

The ceramic tile processing starts with mixing water, masse and marine sludge (by the proportion of %0, %10, %20, %30, %40, and % 50) in a Heidolph mixer at a mixing speed of 160 rpm for 30 minutes. This powder slip was further dried in an oven at 110 °C for 16 hours. The dried powder mixture was crushed in a mortar with a pestle and spread in a steel tray for granulation by spraying water. The water sprayed powder mixture was rotated slowly in a cylindrical container for 30 minutes for granule formation and then dried in an oven at 110 °C for 30 minutes. This granulated powder was pressed at 100 MPa, and further fired at 1000-1200 °C for 1 hour. The sintered tile pellets were finally characterized by various techniques. The tile processing flow sheet is given in Figure 4.1.3.

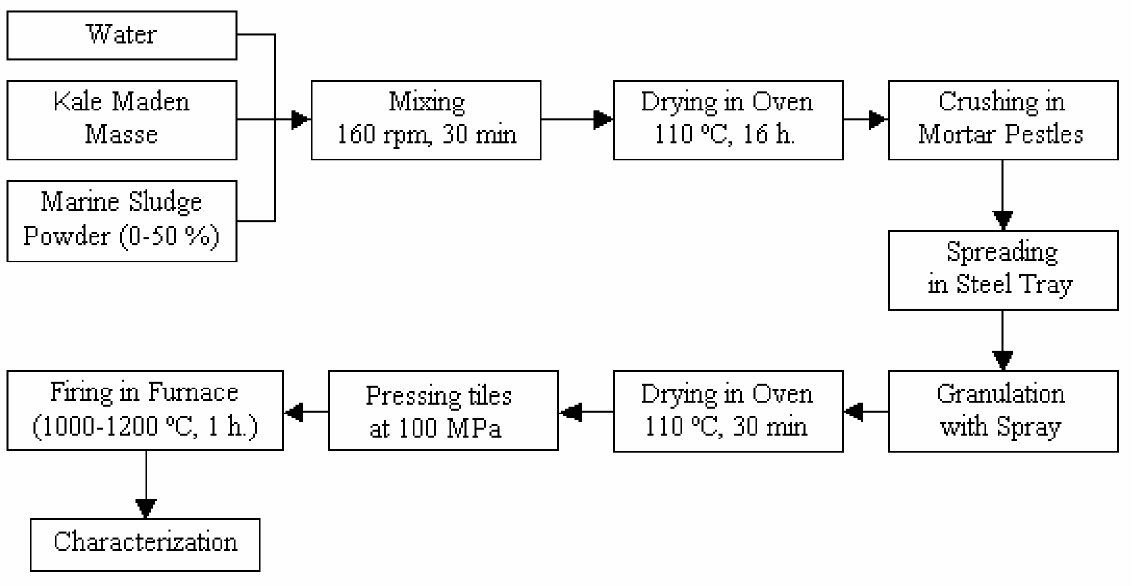


Figure 4.1.3. Processing flow sheet for ceramic tiles containing marine sludge additives.

4.2. Forming and Heat Treatments

Dry pressing was used for the consolidation of tile green pellets. All blends were uniaxially compacted in a hydraulic press (Yıldız Hidrolik-15 tons) under a pressure of 100 MPa in a stainless steel die (diameter: 15mm). A different stainless steel die (diameter: 20 mm) was used for the formation of tiles utilized for compression tests. Rectangular shaped green bodies (85x85x20 mm) were uniaxially compacted by using the same dry press at 45 MPa from 0%, 20%, and 50% marine sludge added powder mixtures.

The sintering of the pellets and tiles were done at varying temperatures (1000-1200^{o}C) in a chamber-type high temperature furnace shown in Figure 4.2.1. (Protherm PLF 160/5-max.1600°C). The soak time was one hour and the heating rate was 10^{o}C/min. The rectangular green tiles were sintered at 1000, 1050, and 1100^{o}C with similar regimes.

Figure 4.2.1. Protherm PLF 160/5- High Temperature Furnace (Max. Temp.=1600°C).

4.3. Characterization

A series of characterization techniques and methods like X- Ray diffraction, DTA/TGA, FTIR, SEM micro-structural analysis, elemental analysis (CHNS determination), water absorption, density measurement, loss on ignition, firing shrinkage, leaching test and mechanical property determination tests were conducted on the powders and sintered tiles. These methods are explained briefly in this section.

The crystallinity and phase structure of the tiles prepared from the marine sludge free masse and the tiles containing 20% and 50% marine sludge fired at 1000, 1100, 1200 °C, shells obtained from sieved marine sludge, treated marine sludge and untreated marine sludge powders were investigated by using an X-Ray Diffractometer (XRD-Philips X'Pert Pro) located in the Center for Materials Research of İYTE with Cu-K_{α} radiation (λ=1.54 A°) in the 2θ interval of 5-70°.

The microstructural features of as-received powders (treated marine sludge and shells), the tiles prepared from treated marine sludge fired at 1050 and 1100^{o}C, and 0%, 20%, and 50% marine sludge containing tiles fired at 1000 and 1100 °C were investigated by using a scanning electron microscope (SEM-Philips XL-30 SFEG) located in the Center for Materials Research of İYTE. Elemental analysis of as-received and the tile samples were conducted by using SEM-Energy Disperse Spectrometry (SEM-EDS). The morphological characterization of the grains and pores were evaluated on polished tile surfaces. The sintered tiles were cut with a diamond saw and cold mounted in polyester for microstructural analysis. Samples were ground with successively sized (240-320-600-800-1200 Grit) silicon carbide papers and polished with diamond suspensions. Polished samples were removed from the mounts. Mounted samples were coated by carbon to avoid charging during SEM analysis.

Thermogravimetric analysis (TGA) was applied on treated marine sludge and shells by using Shimadzu TGA-51/51H . Approximately 10 mg sample was heated at 10 °C/min under 40 ml/min nitrogen and air purge stream up to 1000 °C in the TGA experiments.

IR characterizations were carried out between 400 and 4000 cm^{-1} with Shimadzu FTIR-8201 model Fourier Transformed Infra-red Spectrometer using KBr pellet technique. KBr pellets were prepared by pressing 4 mg sample and 200 mg KBr.

LECO elemental analysis CHNS-932 located in the Center for Materials Research of İYTE was used for the determination of carbon, hydrogen, nitrogen and sulfur contaminations in the treated and untreated marine sludge. It detects them by means of individual, highly selective, infrared detection systems. CHNS (Carbon, Hydrogen, Nitrogen, and Sulfur) is determined simultaneously whereby analysis times are dramatically reduced compared to any sequential system.

The density most commonly determined for a ceramic object is the bulk density, which is the weight divided by the bulk volume. The density and porosity of the samples were determined using Archimedes' technique (ASTM C 20-87). This method involves the determination of the following properties of sintered products: apparent porosity, water absorption, and bulk density. The dry weight of sintered specimens was recorded as the initial step of this method. Each test specimen was boiled for 2 hours in water. After boiling, each specimen was cooled to room temperature while still completely covered with water, and immersed in water for a minimum of 12 hours before weighing. The suspended weight in water of each specimen was measured on the balance with Archimedes' apparatus (Precisa-XP220A). After determining the suspended weight, the specimen was wiped with a wet sponge to remove drops of water from the surface. The damp specimen was then weighed to determine its saturated weight. The density and other properties were determined based on these three weights.

Tiles prepared by 20% and 50% marine sludge additive and without sludge fired at 1000 and 1100 °C were selected for leaching tests. Tile samples were ground by using an agate mortar and the ground powder was sieved by 70-mesh (212 μm) and 50-mesh (300 μm) screens and the powder with particle sizes in between 212-300 μm was further used for the leaching tests. The leach solutions with pH values of 4 and 9 were prepared by using de-ionized water, nitric acid and sodium hydroxide similarly for all tile samples. One gram of ground tile powder in the selected size range was mixed with 75 ml of pH: 4 and pH: 9 leach solutions. The powder suspensions were stirred by a magnetic stirrer for 48 hours and further filtered with a blue-band-filter paper. These clear solutions have been analyzed by using Inductively Coupled Plasma Mass Spectroscopy (ICP- MS Agilent, 7500CE) instrument located in the Environmental Research Center of İYTE. Semi-quantitative analysis was applied on the tile powder fired at 1000 °C with 50% sludge additive leached in solutions at pH: 4 due to the expectation of the highest heavy metal contents for the determination of heavy metal concentration levels. The calibration of the ICP-MS was conducted by using 25 ml of multi element solutions, (ICP Multi element Standard Solution IV CertiPUR®, Merck), (100, 200, 500, 1000, 2000, 5000 and 10000 ppb).

The leaching tests were repeated by increasing the solids content of the leaching solutions (from 75/1 to 3/1) and decreasing the particle size (from 212 μm < d < 300 μm to d<150 μm) in order to increase the metal contents of the clear solutions and to increase the rate of dissolution. Tiles prepared by 20% and 50% marine sludge additive and sludge free tiles fired at 1100 °C were selected for leaching tests. Tile samples were ground by using an agate mortar and the ground powder was sieved by 100-mesh screen and the powder with particle sizes below 150 μm was further used for the leaching tests. The leach solutions with pH values of 4 and 9 were prepared by using de-ionized water, nitric acid and sodium hydroxide similarly for all tile samples. 13 gram of ground tile powder was mixed with 39 ml of leaching solutions (pH: 4 and pH: 9) and were further stirred by a magnetic stirrer for 48 hours. These suspensions were diluted with 195 ml de-ionized water and filtered through a blue-band-filter paper. The resultant clear solutions were analyzed by using Inductively Coupled Plasma Mass Spectroscopy. Semi-quantitative analysis was applied on the tile powder fired at 1100 °C with 50% sludge additive which was expected to have the highest heavy metal contents for the determination of heavy metal concentration levels. The calibration of the ICP-MS was conducted by using 25 ml of multi element solutions, (ICP Multi element Standard

Solution IV CertiPUR®, Merck), (1, 5, 10, 20, 50, 100, 200, 500, 1000, 2000 and 5000 ppb).

4.4. Determination of Mechanical Properties

Compression tests were conducted on tiles which were pressed with the 15 mm stainless steel die from 0, 10, 20, 30, 40 and 50% marine sludge added powder mixtures and fired at 1000, 1050, 1075 and 1100 °C. Compression testing in this work was conducted by Shimadzu AG1 250 KN instrument located in the Center for Materials Research of İYTE.

A rubber sheet was placed on the top and bottom surfaces of the cylindrical specimen to avoid stress concentration during compressive loading of the brittle specimen. A second set of compression tests were conducted on tiles which were pressed with a 20 mm stainless steel die from 0%, %20 and %50 sludge added powders and fired at 1000, 1050, 1100 °C. Tests were repeated on three tiles for each compression testing experiment.

All tile samples were cleaned with water after grinding and immersed in an ultrasonic bath and were further dried at 110 °C for 2 h before each compression test. After samples were carefully centered in the machine between the contact blocks, the load was applied on the samples continuously until ultimate failure.

CHAPTER 5

RESULTS AND DISCUSSION

The results on the characterization of the raw materials and the tile samples are given in two separate sections in this chapter. The results of the characterization studies conducted on the sludge and shells are discussed in the first part of the chapter. The properties of the ceramic tiles are given in the second section. The results of the leaching tests and the mechanical testing are also given in this part of the thesis.

5.1. Characterization of the Raw Materials

The untreated marine sludge, treated marine sludge and also sintered marine sludge were characterized by XRD, FTIR, TGA, CHNS Determination and SEM (EDX and mapping study) along with the determination of loss on ignition, firing shrinkage, density measurements of green and sintered tiles fired at 1000 °C, 1050 °C and 1100 °C. Shells present in the sludge were investigated by XRD, TGA, SEM and EDS in order to understand their probable effects on tile processing.

A preliminary simple experiment was conducted for the determination of the approximate water content of the untreated marine sludge where 50 grams of the sludge was placed in an oven at 140 °C for 5 hours. Water content was estimated to be about 62 % from the dried weight.

Untreated marine sludge can be defined as the sludge which was dredged, sorted roughly from shells, dried at 110 °C in an oven and finally ground in a mortar with a pestle in this work.

The examination of the XRD patterns given in Figure 5.1.1 have shown that there were no significant differences between untreated and treated marine sludge except the presence of Halite phase (a crystalline phase of sodium chloride) in the untreated sludge. XRD analysis had shown that the marine sludge contains Aragonite (a different form of Calcium Carbonate), illite, quartz (SiO_2), and mica phases which are commonly used conventional ceramic raw materials. The results of XRD analysis did not indicate the presence any heavy metal containing phases in the untreated and treated sludge samples.

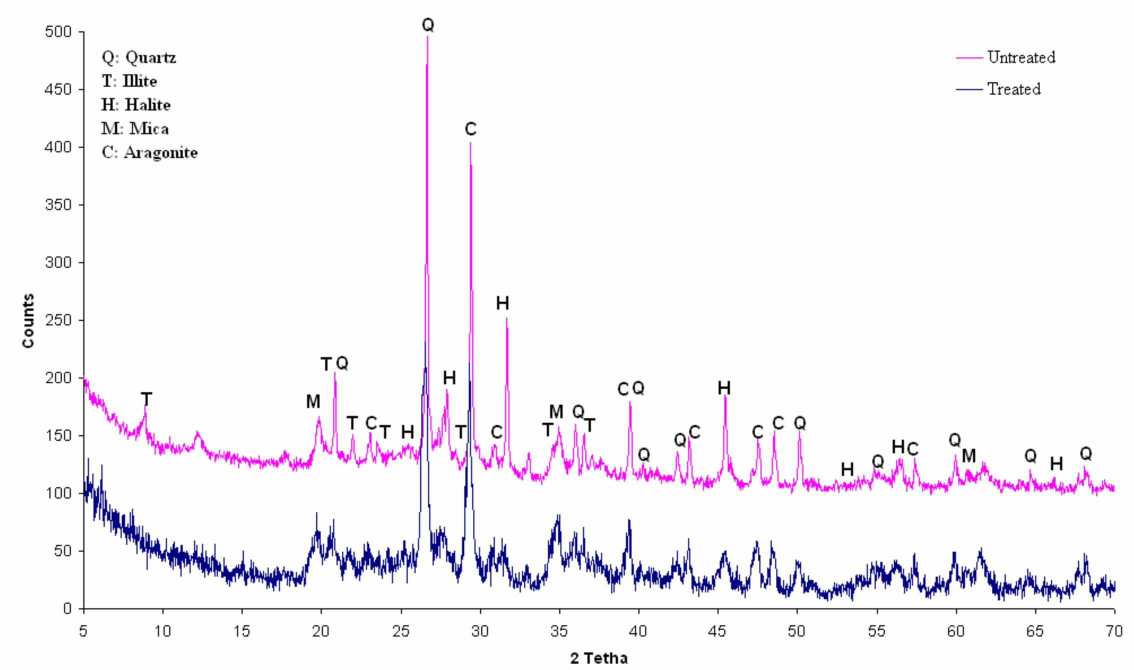


Figure 5.1.1. XRD chart of the untreated and treated marine sludge.

Treated marine sludge was also characterized by using several techniques after pretreatment explained in Chapter 4. The salt content of the sludge was significantly reduced after pretreatment as indicated by the absence of halite peaks in the XRD pattern. The calcium carbonate content originating from the presence of shells was not significantly affected by the pretreatment.

The untreated marine sludge content is unknown and complicated and thus the interpretation of the FTIR characterization results given in Figure 5.1.2 is relatively very hard.

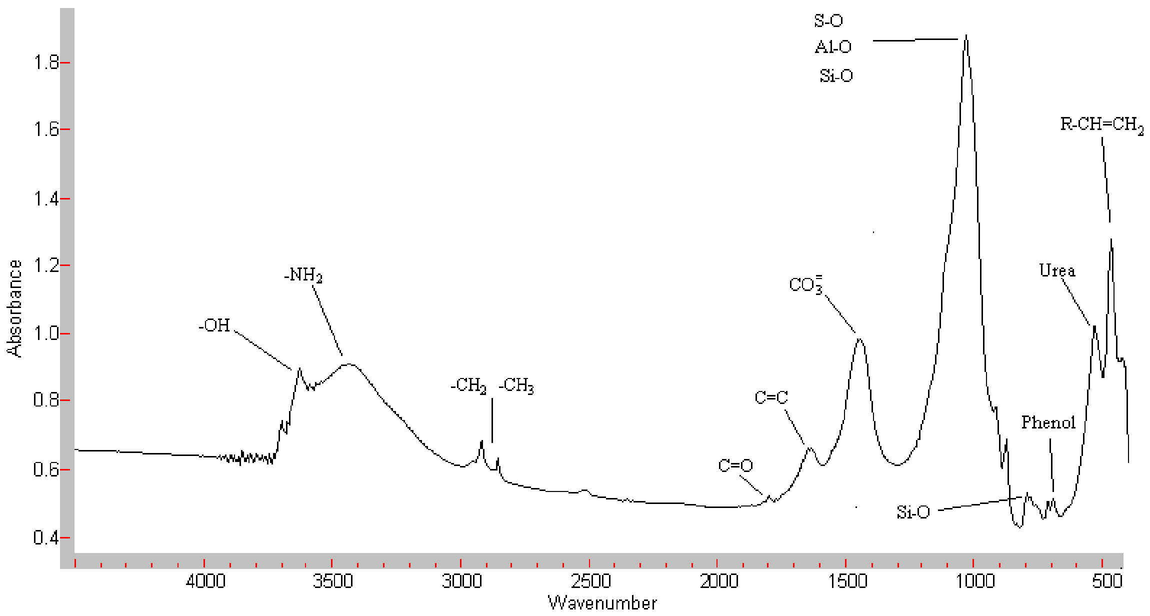


Figure 5.1.2. FTIR spectrum of untreated marine sludge.

The 530 cm^{-1} peak and 695 cm^{-1} in Figure 5.1.2 show that there are urea coming from sewage in marine sludge and phenol respectively. The 1030 cm^{-1} peak shows that sludge heavily contains compounds with Al-O bonds indicating presence of Al_2O_3 or $Al(OH)_3$ and Si-O bonds indicating the presence of SiO_2. The 1446 cm^{-1} peak shows $CO_3^{=}$ indicating most probably $CaCO_3$. Other peaks at 469, 795, 1634, 2919, 3436 and 3618 cm^{-1} show the presence of some organic compounds for which the chemical nature is unknown in the sludge structure.

Treated marine sludge TGA experiments were carried out under nitrogen and air purge both at 40 ml/min. Oxidation may occur in air which may yield different TGA curves originating from differences between oxidation and decomposition behavior of the organics as seen in Figure 5.1.3. Similar total weight loss of about 18% was observed in both environments at 1000 °C.

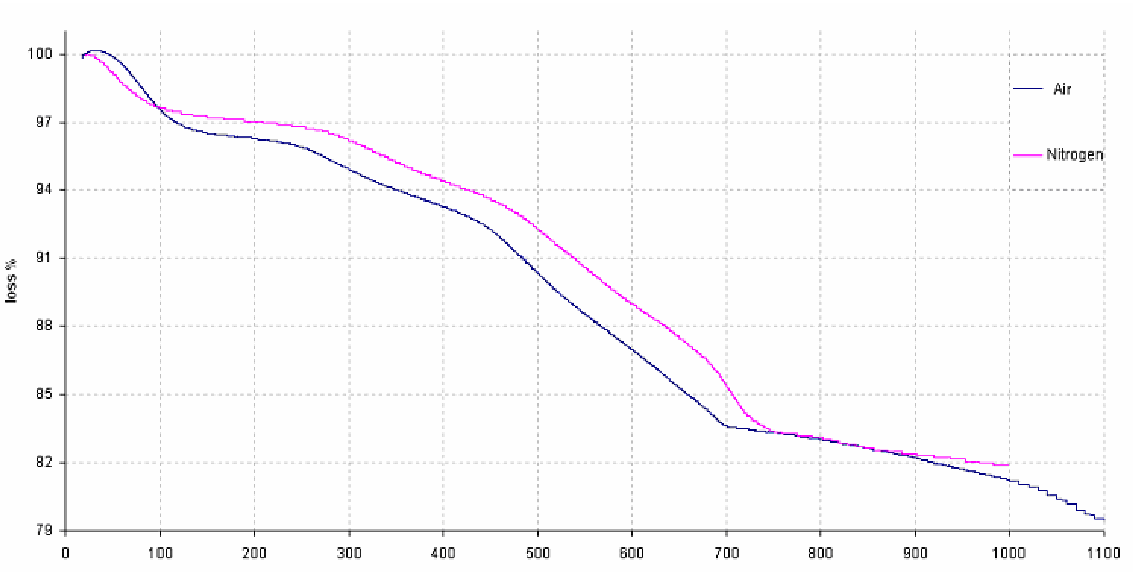


Figure 5.1.3. TGA curve of treated marine sludge.

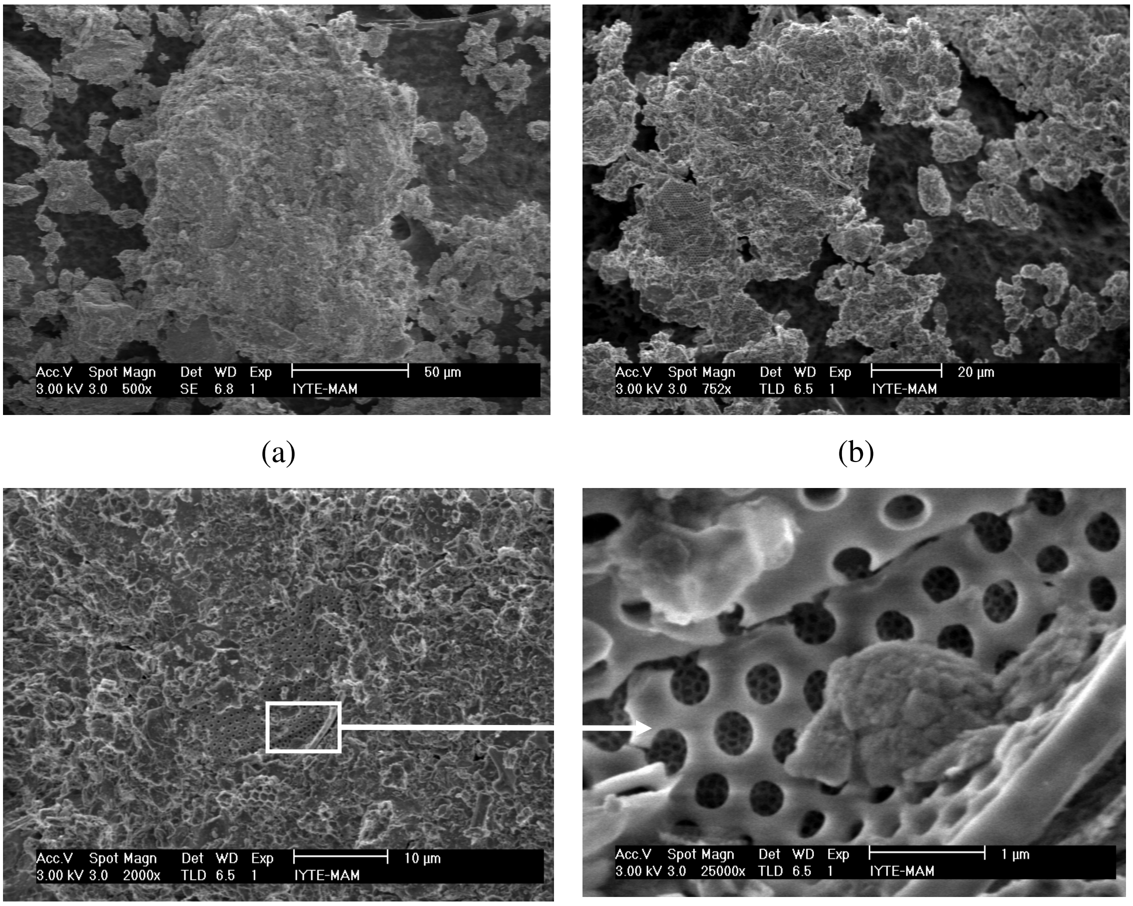
The weight loss started at around 25 °C, occurred in a number of stages up to 1100°C and about 21 % of the sludge weight was lost under air flow. The first 3% decrease in the mass occurred in between 25 and 200 °C due to the removal of physical water. The second relatively slower mass loss was observed in the 220 – 430 °C range most probably due to the decomposition/oxidation of organic compounds containing sulphur and nitrogen. The third mass loss stage was observed in the 480– 700 °C range which may be due to the removal of crystal water and the decomposition of carbonates. The weight loss observed above 700 °C up to 1100 °C for the air flowing run may be due to the decomposition of aragonite in the residual sea shells.

The amount of carbon, hydrogen, nitrogen and sulphur present in the sludge was determined by Elemental Analysis (CHNS determination). The results of elemental analysis are given in Table 5.1.1. In TGA result, the 21 % of the sludge was lost and about 4 % were humidity. The carbon content was partially due to the presence of aragonite and partially due to the present organic structure. Total amount of CHNS was 6.54 and 6.48 for untreated marine sludge and treated marine sludge, respectively.

Table 5.1.1. Results of the elemental analysis (CHNS Determination) (UMS: Untreated marine sludge and TMS: Treated marine sludge).

	UMS	**T MS**
%C	4.42	4.31
%H	0.85	0.84
%N	0.33	0.32
%S	0.94	1.00
Total	6.54	6.48

SEM investigation of the treated marine sludge powder sample given in Figure 5.1.4 revealed the presence of marine life residues shown in Figure 5.1.4 c and 5.1.4 d which are known as diatom. These diatom fossils may be the source of calcium carbonate which was most likely crushed during processing/grinding.



(a) (b)

(c) (d)

Figure 5.1.4. SEM images of the treated marine sludge at (a) 500X, (b) 752X, (c) 2000X and (d) 25000X.

EDX Analysis was applied on treated marine sludge. Aluminum and silicon were detected as the major metal ions and other elements were detected in less than 5 At. % levels. Pb and Hg were observed to be in significant levels in the same analysis and they are commonly known to be dangerous and poisonous elements as given in Figure 5.1.5 and Table 5.1.3. This observation supports the goal of this thesis work on immobilizing these heavy metals present in the dredged waste sludge in a ceramic tile structure.

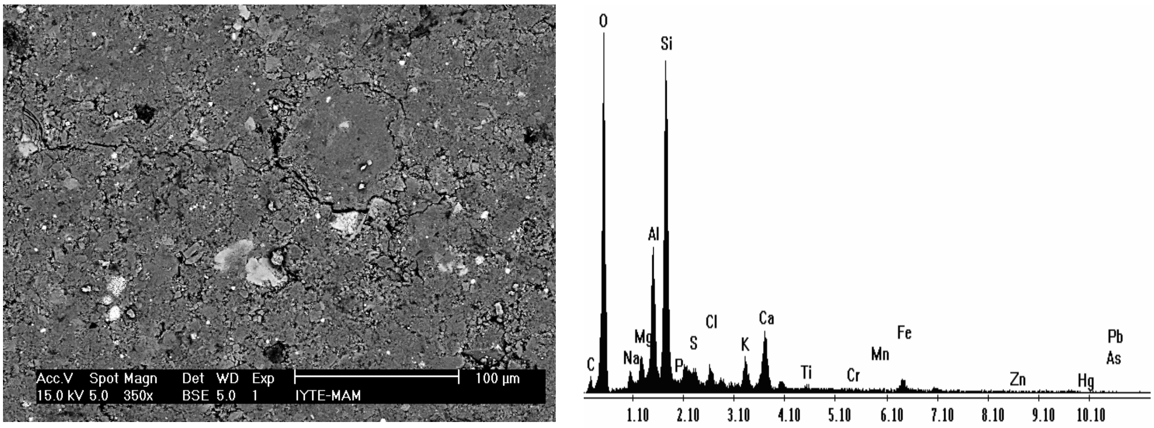


Figure 5.1.5 EDX results of the treated marine sludge pellet.

Table 5.1.3 EDX results of the treated marine sludge pellet.

Element	C	Na	Mg	Al	Si	P	S	Ca	Cr	Mn	Fe	Zn	Hg	Pb
Wt %	3,52	0,61	1,40	5,07	11,93	0,41	0,84	4,54	0,32	0,43	3,05	1,05	12,71	23,12
At %	9,40	0,85	1,84	6,02	13,62	0,42	0,84	3,63	0,20	0,25	1,75	0,52	2,03	3,58

In Scanning Electron Microscope (SEM) data on more than 15 elements can be collected simultaneously and be used to generate X-ray dot maps displaying the spatial distribution of the elements in the sample. This technique was also applied on the treated marine sludge pellet. The results of this study are shown in Figure 5.1.6.

The mapping of Na, Mg, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Zn, Hg and Pb were performed in the above figure. It is evident from this mapping study that Na, P, S, Ca and Fe distributions are not uniform where locally concentrated regions are present. The Hg and Pb distributions were uniform with the absence of locally concentrated regions.

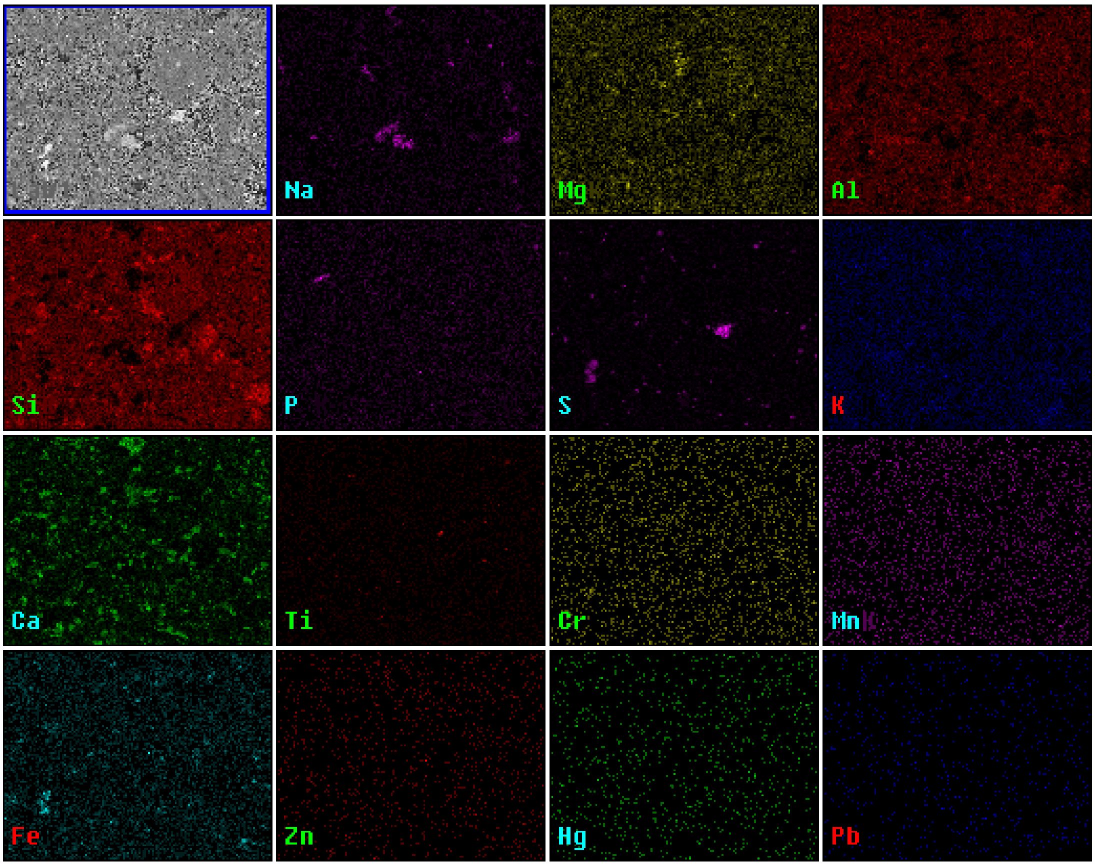


Figure 5.1.6. Mapping study of marine sludge pellet.

Treated marine sludge pellets were sintered at 1000 (MS1000), 1050 (MS1050) and 1100 (MS1100) °C. Green density of marine sludge pellets was estimated to be 1.9 g/cm^3 from their dimensions and weight.

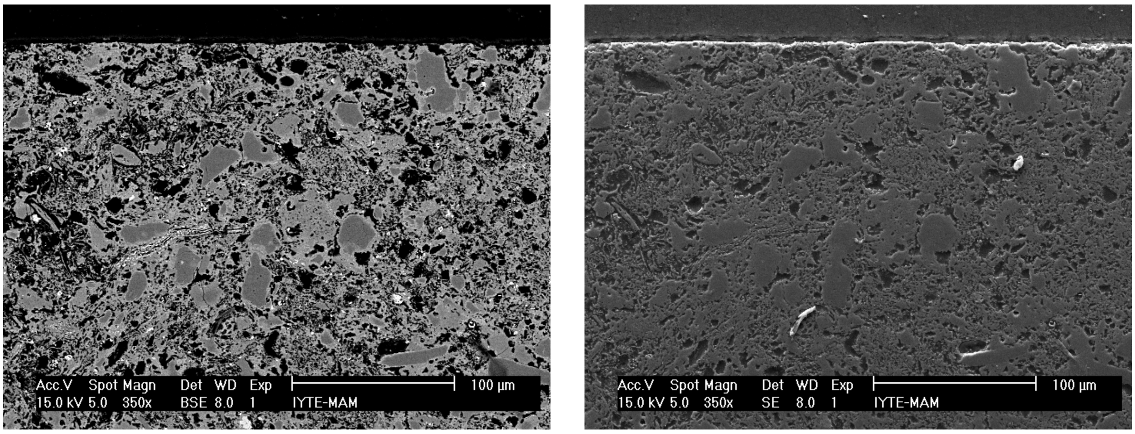
Loss on ignition, linear firing shrinkage and bulk density values were determined and are given in Table 5.1.4. Loss on ignition values increase with the sintering temperature and agrees well with the TGA results. The differences between the 1050 and 1100 °C firing shrinkages are significantly higher when compared with the 1000-1050 °C shrinkages. It is interesting to note that bulk density values of samples sintered at 1000 and 1050 °C are smaller than their green densities. It means that volume did not change so much while weight decreased during sintering but at 1100 °C the volume of the pellets decreased considerably.

Table 5.1.4. Sintered marine sludge pellet properties.

Sample	**Loss on ignition, %**	**Linear firing shrinkage, %**	**Bulk density g.cm^{-3}**
MS1000	18.4	0.39	1.56
MS1050	19.3	1.53	1.61
MS1100	21.4	9.71	2.06

The 1050 and 1100 °C sintered marine sludge pellets were investigated by SEM/EDX using SE and BSE modes. BSE mode provides chemical information from the specimen's surface.

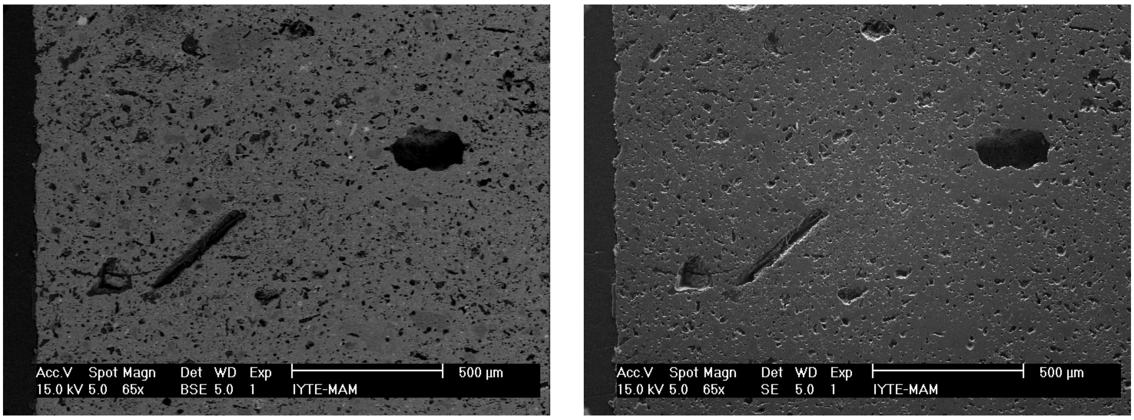
Color differences in Figure 5.1.7.a and 5.1.8.a indicates that there is no homogeneity in view of chemical composition. This heterogeneity could be prevented by well-mixing of powder samples before sintering.



(a) (b)

Figure 5.1.7. SEM images of the sludge pellet sintered at 1050 °C with (a) BSE and (b) SE modes at 350X.

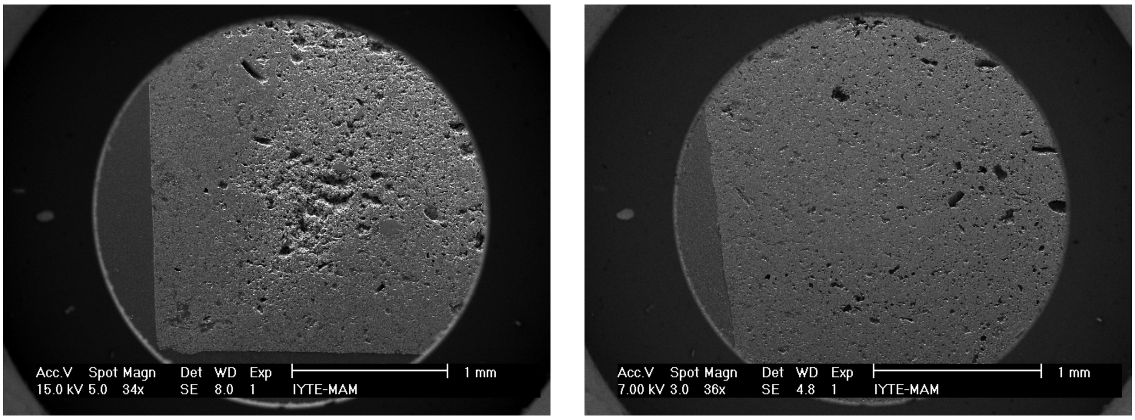
The SEM images given in Figures 5.1.7 and 5.1.8 indicated the presence of considerable amount of porosity for both sintering temperatures. The sludge pellet sintered at 1050 °C seems to have considerably higher porosity content when compared with the 1100 °C sintered pellet. These microstructural observations from the SEM images are in agreement with the determined firing shrinkages.



(a) (b)

Figure 5.1.8. SEM images of the sludge pellet sintered at 1100 °C with (a) BSE (b) SE modes at 65X .

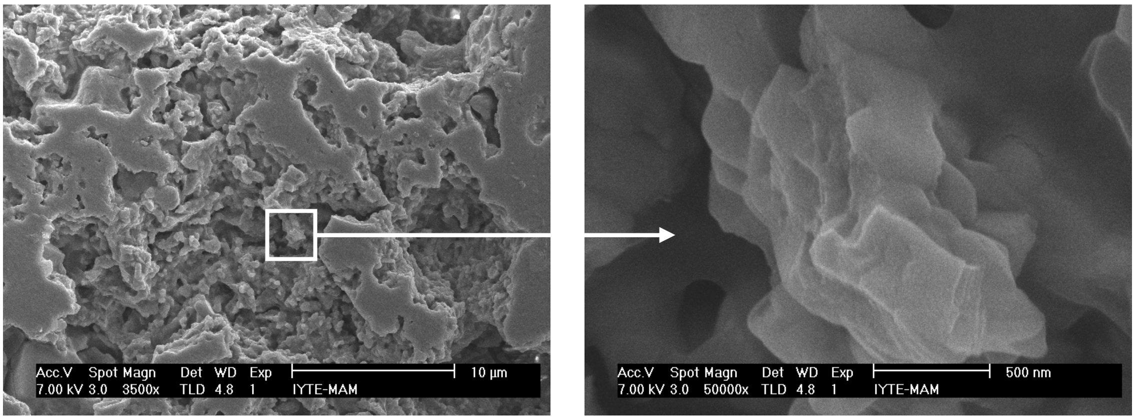
The low magnification SEM pictures of the pellets given in Figure 5.1.9 indicated the presence of nonuniform porosity in the radial direction. This may be related with the differences in the powder packing during uniaxial dry pressing and the subsequent gas evolution during heating to the soak temperature. This nonuniformity was more pronounced at 1050 °C and the microstructure becomes more uniform with the increase of the sintering temperature to 1100 °C.



(a) (b)

Figure 5.1.9. SEM image of sintered sludge at (a) 1050 °C and (b) 1100 °C with SE mode of 34X.

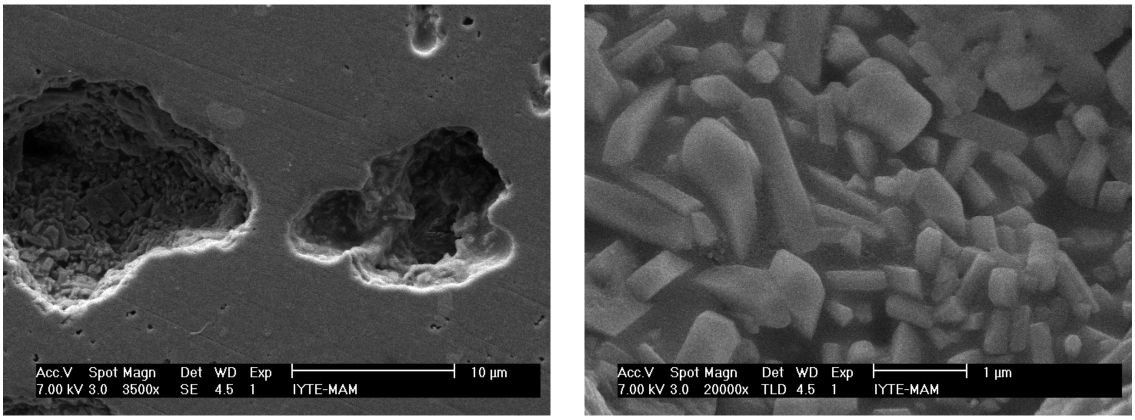
The higher magnification images given in Figure 5.1.10 indicated the presence of fine grained microstructure along with relatively large pores originating most likely from the removal of volatile compounds and the decomposition of carbonates in the green structure.



(a) (b)

Figure 5.1.10. SEM image of sintered at 1050 °C sludge with TLD detector at (a) 3500X and (b) 50000X.

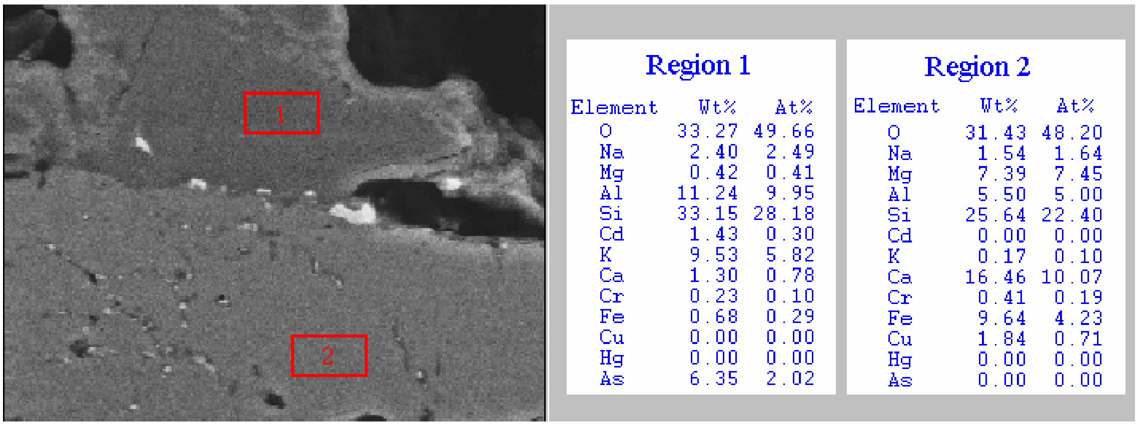
Grains with sizes in the 0.5-1.5 µm range can be seen in Figure 5.1.11b in the microstructure of the 1100 °C sintered marine sludge pellet.



(a) (b)

Figure 5.1.11. SEM image of sintered at 1100 °C sludge at (a) 3500X and (b) 50000X.

EDX was applied on sintered sludge at 1050 and 1100 °C. EDX analysis of the 1050 °C sintered sludge pellet was performed on two different regions (dark and bright) as seen from Figure 5.1.12. Si, Al and K were mainly determined and As which is a poisonous element also was determined in region 1. Si, Ca, Al, Mg and Fe were determined in region 2 where no Hg and As were detected.



Region 1

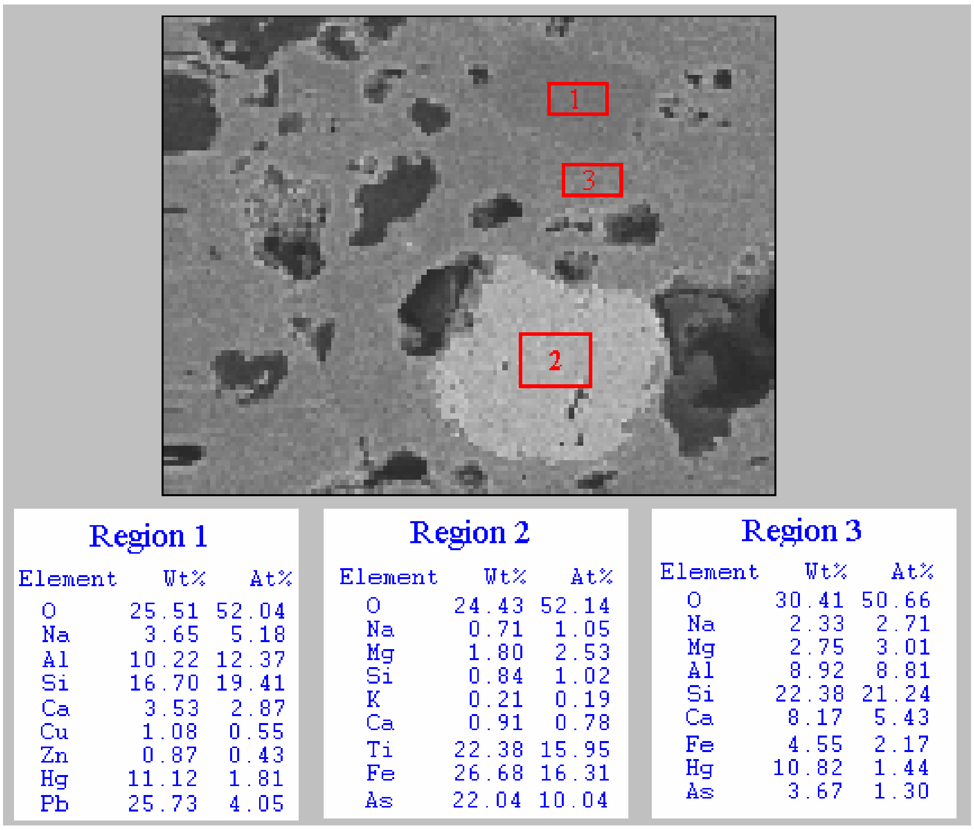
Element	Wt%	At%
O	33.27	49.66
Na	2.40	2.49
Mg	0.42	0.41
Al	11.24	9.95
Si	33.15	28.18
Cd	1.43	0.30
K	9.53	5.82
Ca	1.30	0.78
Cr	0.23	0.10
Fe	0.68	0.29
Cu	0.00	0.00
Hg	0.00	0.00
As	6.35	2.02

Region 2

Element	Wt%	At%
O	31.43	48.20
Na	1.54	1.64
Mg	7.39	7.45
Al	5.50	5.00
Si	25.64	22.40
Cd	0.00	0.00
K	0.17	0.10
Ca	16.46	10.07
Cr	0.41	0.19
Fe	9.64	4.23
Cu	1.84	0.71
Hg	0.00	0.00
As	0.00	0.00

Figure 5.1.12. EDX result of the sludge sintered at 1050 °C

EDX analysis of the 1100 °C sintered sludge pellet was conducted on three regions as given in Figure 5.1.13. In region 1 (or dark region), Al, Si, Hg and Pb were mainly determined and it seemed that Hg and Pb were successfully kept in the structure. In region 2, Fe, Ti and As were mainly observed. And in region 3, Si, Al, Ca and Hg were observed and it seemed that Hg and Pb were kept in sintered structure, too.



Region 1

Element	Wt%	At%
O	25.51	52.04
Na	3.65	5.18
Al	10.22	12.37
Si	16.70	19.41
Ca	3.53	2.87
Cu	1.08	0.55
Zn	0.87	0.43
Hg	11.12	1.81
Pb	25.73	4.05

Region 2

Element	Wt%	At%
O	24.43	52.14
Na	0.71	1.05
Mg	1.80	2.53
Si	0.84	1.02
K	0.21	0.19
Ca	0.91	0.78
Ti	22.38	15.95
Fe	26.68	16.31
As	22.04	10.04

Region 3

Element	Wt%	At%
O	30.41	50.66
Na	2.33	2.71
Mg	2.75	3.01
Al	8.92	8.81
Si	22.38	21.24
Ca	8.17	5.43
Fe	4.55	2.17
Hg	10.82	1.44
As	3.67	1.30

Figure 5.1.13. EDX result of the sludge sintered at 1100 °C.

The separated shell pieces from the sludge were characterized by XRD, TGA, SEM and EDX for obtaining some information about their structure. The XRD pattern given in Figure 5.1.14 indicated that the shells were mainly formed from the calcium carbonate phases of aragonite and calcite.

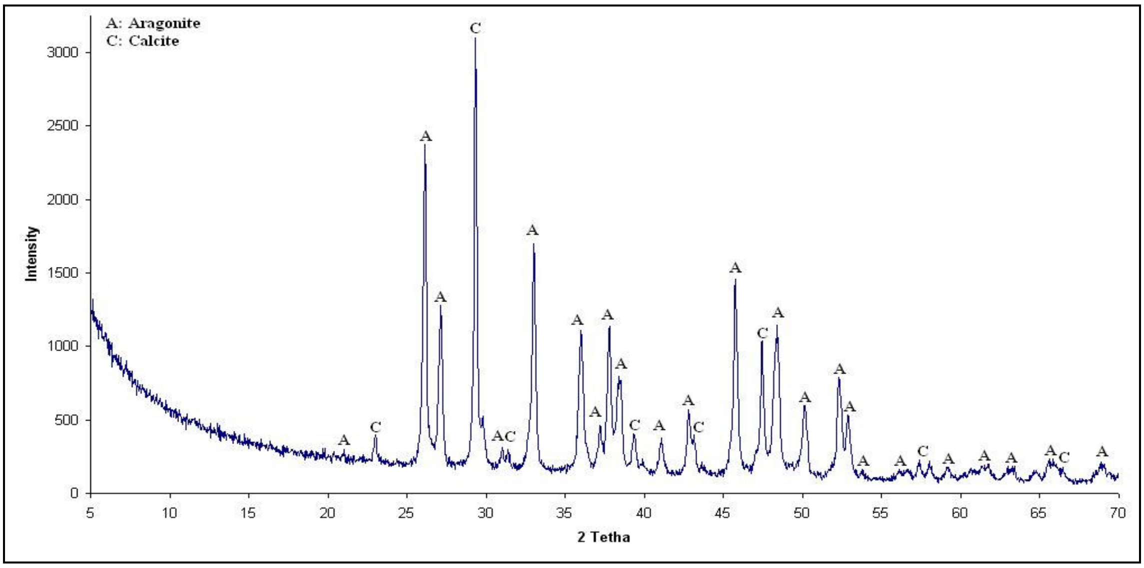


Figure 5.1.14. XRD chart of the shells

The TGA curve given in Figure 5.1.15 also supported the above results. The weight loss occurred mainly in the 600-775 °C range and a final total weight loss of 38% was observed for the powdered shell sample where a stoichiometrically pure $CaCO_3$ would give a final weight loss of 40%.

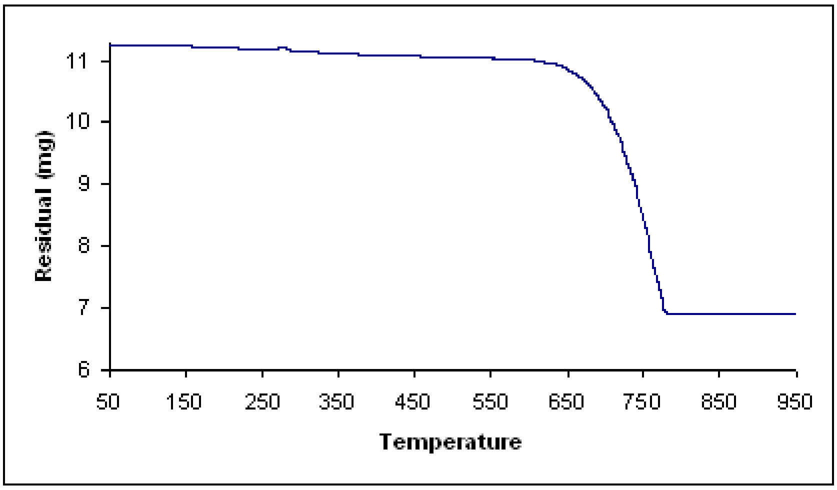
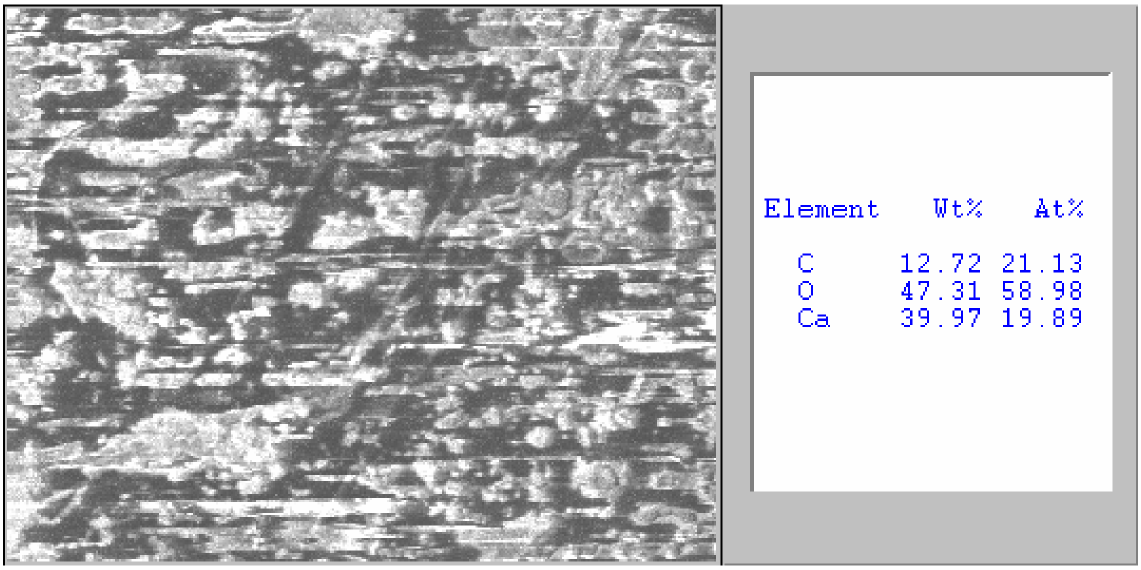


Figure 5.1.15. TGA curve of shells

The EDX analysis given in Figure 5.1.16 also indicated that the shells were mainly formed from the calcium carbonate.



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Element    Wt%    At%

  C      12.72  21.13
  O      47.31  58.98
  Ca     39.97  19.89
```

Figure 5.1.16. EDX result of shells.

5.2. Characterization of the Marine Sludge Added Sintered Tiles

The microstructure and the nature of the phases present in the sintered ceramic tiles were investigated by SEM-EDX and XRD. The water absorption, density and firing shrinkage of the sintered pellets were determined by using Archimedes method and pellet dimensions/weight. Leaching tests were performed on the tile samples in order to investigate the level of immobilization of heavy metals in the structure. Mechanical properties of the tiles were determined under compression.

5.2.1. Microstructure and Phase Analysis

The microstructural features of 0%, %20, %50 sludge added tile pellets sintered at 1000 and 1100 °C were investigated by using SEM pictures given in Figure 5.2.1.1 Elemental analysis of the selected regions of the sintered tiles were conducted by using SEM-EDX. The morphological characterization of the grains and pores were evaluated on polished tile surfaces. Sintered tile specimens were cut with a diamond saw and cold mounted in polyester SEM investigation. Samples were ground with successively sized

(240-320-600-800-1200 Grit) silicon carbide papers and polished with diamond suspensions. Polished samples were removed from the mounts. Mounted samples were coated by carbon to avoid charging during SEM analysis.

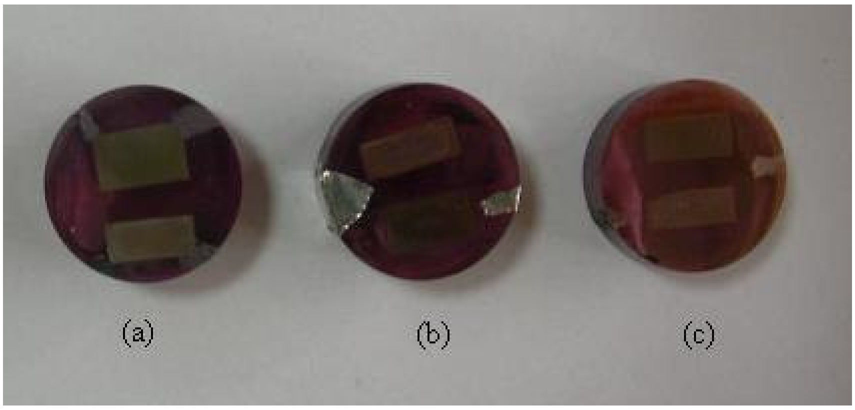
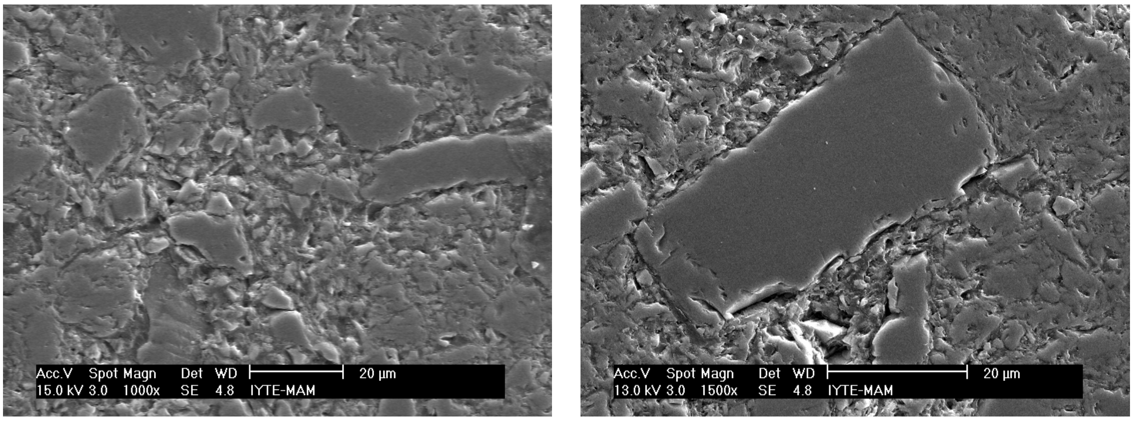


Figure 5.2.1.1. Samples prepared for SEM examination: a) pellet without additives and fired at 1000 °C and 1100 °C, b) pellets containing %20 sludge additives and fired at 1000 °C and 1100 °C, c) pellets containing %50 sludge additives and fired at 1000 °C and 1100 °C.

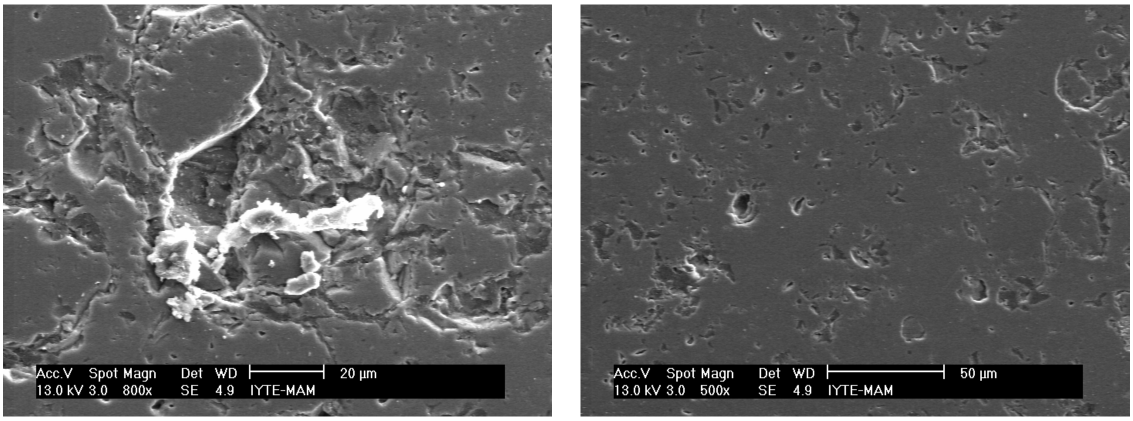
SEM image of tile without sludge at 1000 °C (a) 1000X and (b) 1500X indicate that vitrification was not begun as given in Figure 5.2.1.2. It is evidence to show that there is the particle which has particle size about 40 µm (Figure 5.2.1.2 b).



(a) (b)

Figure 5.2.1.2. SEM image with SE mode of tile without sludge fired at 1000 °C at (a) 1000X and (b) 1500X.

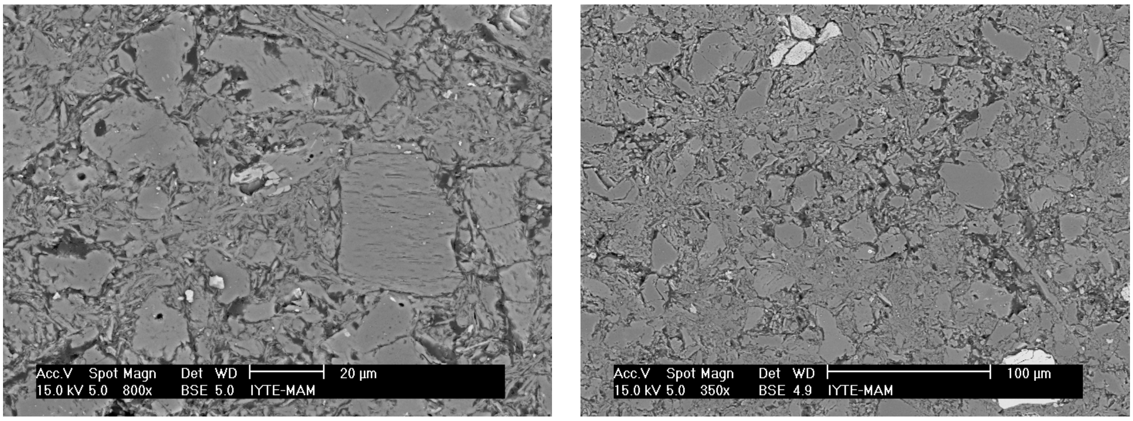
SEM image of tile without sludge at 1100 °C at (a) 800X and (b) 500X show that vitrification was almost begun as seen from Figure 5.2.1.3 although there are some porosity.



(a) (b)

Figure 5.2.1.3. SEM image with SE mode of tile without sludge fired at 1100 °C at (a) 800X and (b) 500X in different area.

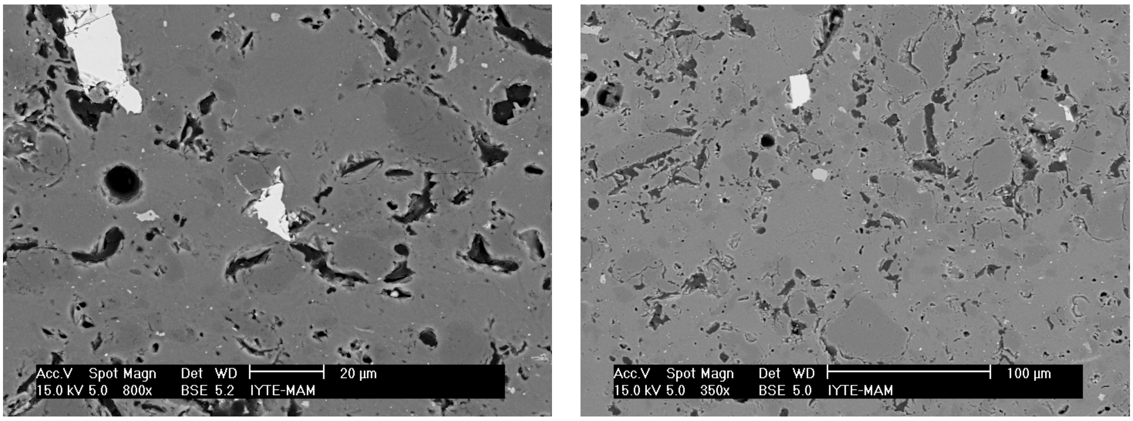
BSE mode gives information about chemical composition differences in structure. In Figure 5.2.1.4, it can be seen that there are some particle which are considerable bigger than other particle. Moreover, there are some particles having bright area.



(a) (b)

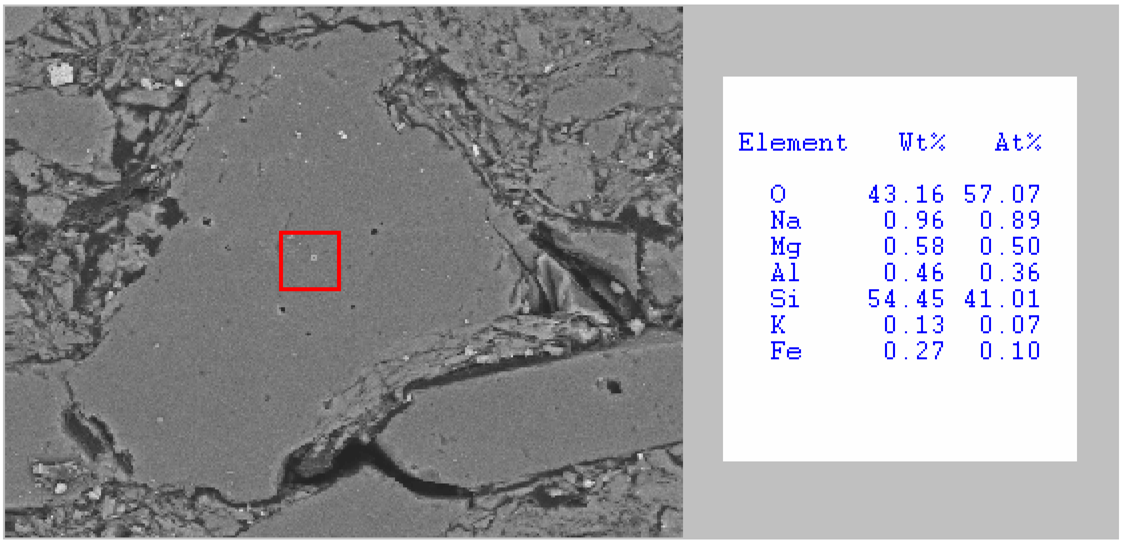
Figure 5.2.1.4. SEM image with BSE mode of tile without sludge at 1000 °C at (a) 800X and (b) 350X in different area.

In Figure 5.2.1.5, it can be seen that particles almost disappeared but there is still color differences. Moreover, large pores were observed to have a diameter approximately 10 µm. It means that vitrification was not completed yet.



(a) (b)

Figure 5.2.1.5. SEM image with BSE mode of tile without sludge fired at 1100 °C at (a) 800X and (b) 350X.



Element	Wt%	At%
O	43.16	57.07
Na	0.96	0.89
Mg	0.58	0.50
Al	0.46	0.36
Si	54.45	41.01
K	0.13	0.07
Fe	0.27	0.10

Figure 5.2.1.6 EDX result of the tile without additives fired at 1000 °C.

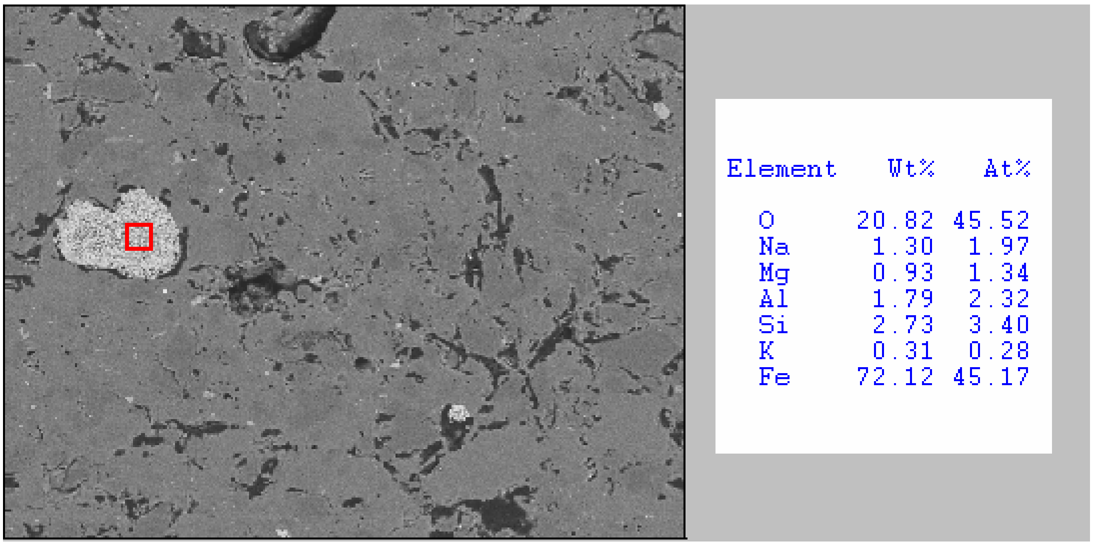
EDX was applied on one of the big particles in the structure of the tile without additives fired at 1000 °C. Chemical composition of this particle was determined as SiO_2 as given in Figure 5.2.1.6.

EDX analysis given in Table 5.2.1.1. conducted on five different areas shows that average atomic percentage value of Al and Si were 10.1 and 29.1. Na, Mg, K and Fe were detected but average atomic percentage value for these elements were less than 5 %.

Table 5.2.1.1. EDX analysis of the tile without additives fired at 1000 °C in five different area.

	O	Na	Mg	Al	Si	K	Fe
average	54.9	2.2	0.9	10.1	29.1	1.9	0.8
std-dev	1.5	0.2	0.1	0.6	1.5	0.3	0.2

EDX study was also performed with one of the bright particles in the structure of the tile without additives fired at 1100 °C. Chemical composition of this particle was determined as Fe and O (maybe FeO) as given in Figure 5.2.1.7.



Element	Wt%	At%
O	20.82	45.52
Na	1.30	1.97
Mg	0.93	1.34
Al	1.79	2.32
Si	2.73	3.40
K	0.31	0.28
Fe	72.12	45.17

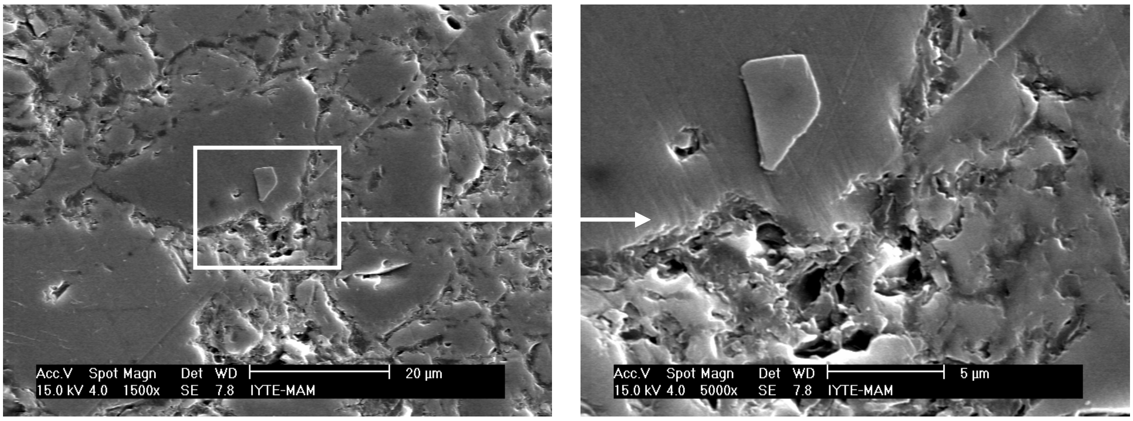
Figure 5.2.1.7 EDX result of the tile without additives fired at 1100 °C.

EDX analysis conducted on five different areas indicates that average atomic percentage value of Al and Si were 9.84 and 30.22. Na, Mg, K and Fe were detected but average atomic percentage value for these elements were less than 5% as given in Table 5.2.1.2.

Table 5.2.1.2. EDX analysis of the tile without additives fired at 1100 °C in five different areas

	O	Na	Mg	Al	Si	K	Fe
average	54.02	2.33	0.74	9.84	30.22	1.90	0.95
std-dev	0.43	0.22	0.07	0.34	0.50	0.03	0.34

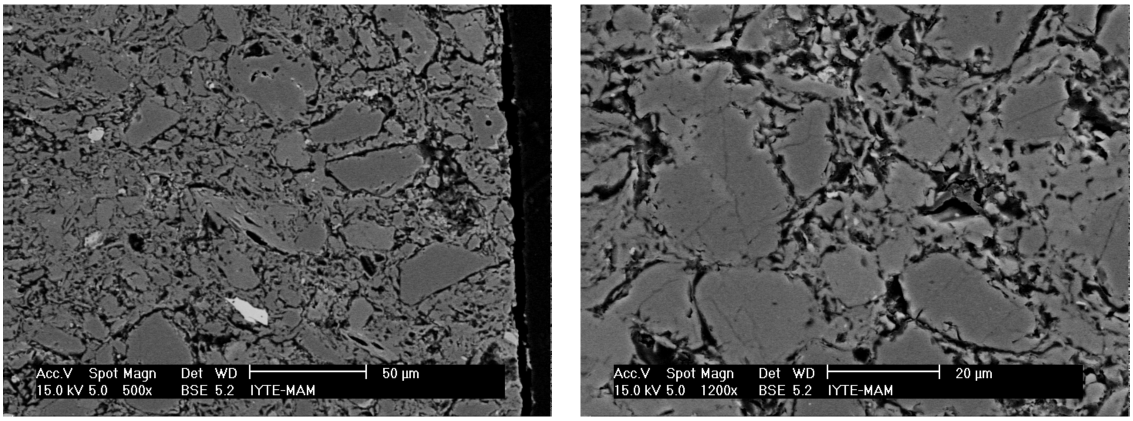
In the SEM results of the tile containing 20 % marine sludge additives, so much difference were not observed with the tile without marine sludge additives. Figure 5.2.1.8 shows that it seems this tile were more vitrified than the tile without additives.



(a) (b)

Figure 5.2.1.8. SEM images with SE mode of 20 % sludge added tile fired at 1000 °C at (a) 1500X and (b) 5000X in same area.

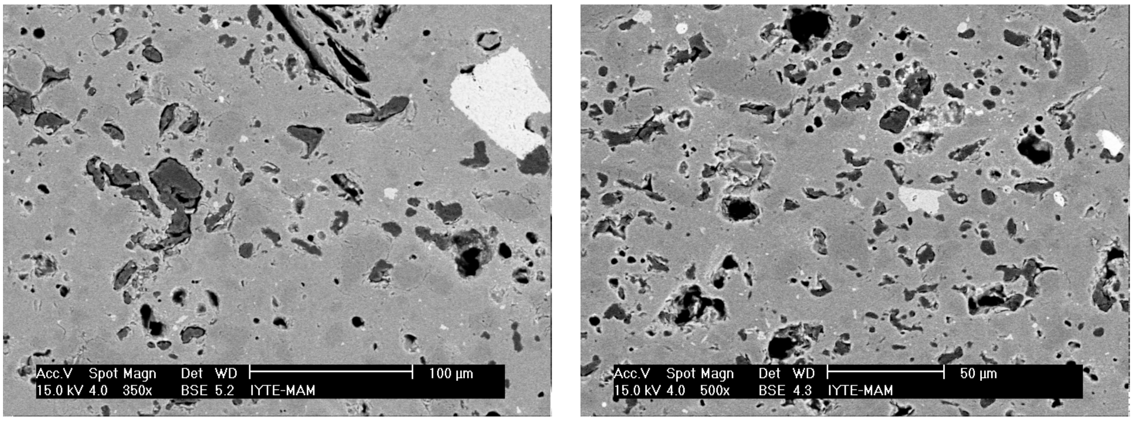
SEM image with SE mode of tile containing 20 % sludge additives fired at 1000 °C indicates that firing at 1000 °C were not sufficient for sintering even if marine sludge additives was added as given in Figure 5.2.1.9.



(a) (b)

Figure 5.2.1.9. SEM images with BSE mode of 20 % sludge added tile fired at 1000 °C at (a) 500X and (b) 1200X.

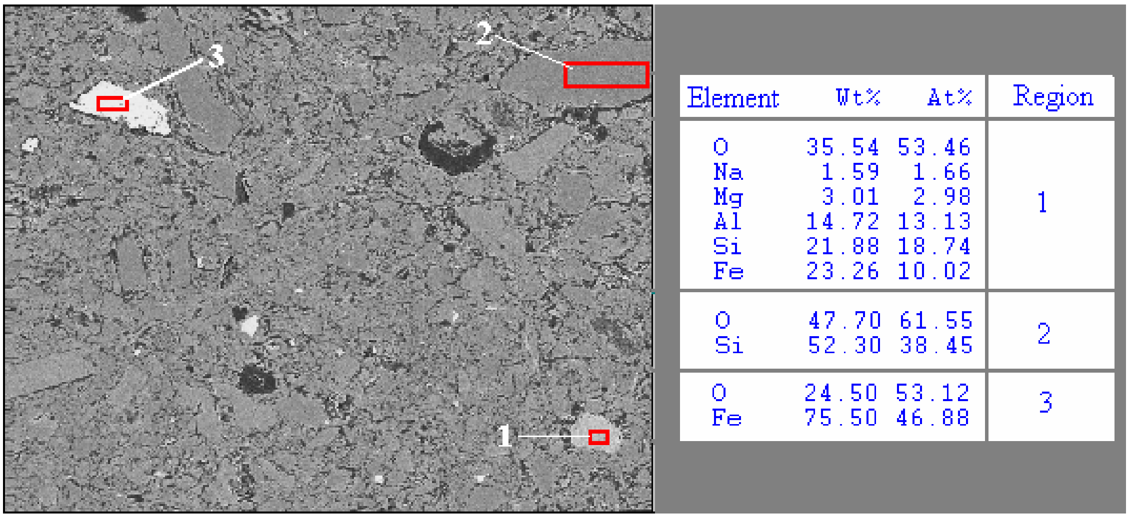
The SEM images with BSE mode of the tile containing 20 % sludge additives fired at 1100 °C given in Figure 5.2.1.10 shows that there are three different areas with different brightness along with some porosity in the structure. Pores were observed to have a diameter of approximately 10 µm. The SEM examination indicated that the structure was densified at this firing temperature.



(a) (b)

Figure 5.2.1.10. SEM images with BSE mode of 20 % sludge added tile fired at 1100°C at (a) 350X and (b) 500X.

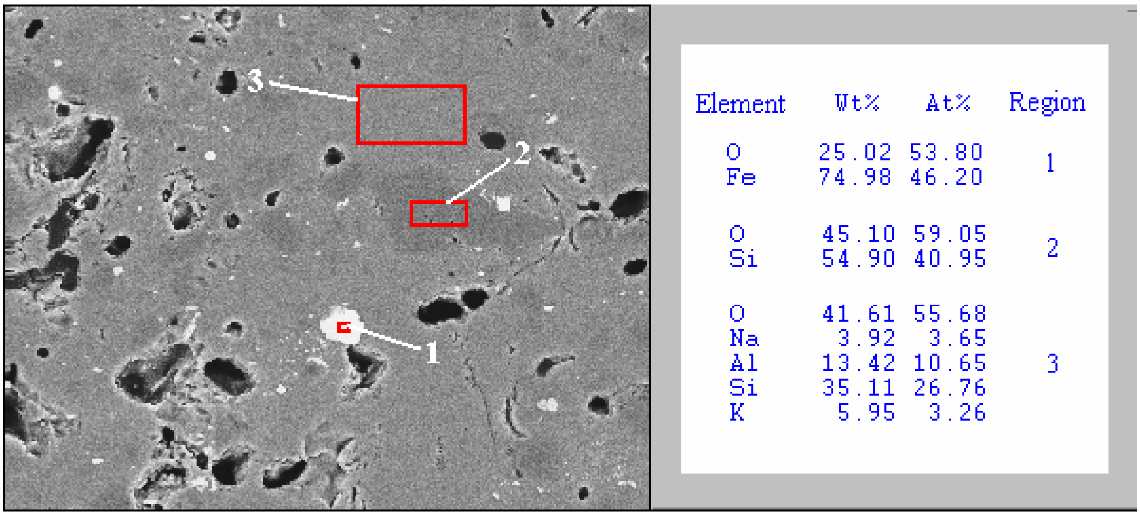
Al, Si and Fe were mainly determined in region 1 in the EDX analysis of the tile containing 20 % sludge additives fired at 1000 °C. Si in the form of SiO_2 was observed in region 2 and Fe was found in region 3 as seen from Figure 5.2.1.11.



Element	Wt%	At%	Region
O	35.54	53.46	1
Na	1.59	1.66	
Mg	3.01	2.98	
Al	14.72	13.13	
Si	21.88	18.74	
Fe	23.26	10.02	
O	47.70	61.55	2
Si	52.30	38.45	
O	24.50	53.12	3
Fe	75.50	46.88	

Figure 5.2.1.11. EDX result of 20 % sludge added the tile fired at 1100 °C.

In EDX analysis of tile containing 20 % sludge additives fired at 1100 °C, Fe was found in region 1. Si most likely in the form of SiO_2 was observed in region 2 and Al, Si and K were mainly determined in region 3 as seen from Figure 5.2.1.12.



Element	Wt%	At%	Region
O	25.02	53.80	1
Fe	74.98	46.20	
O	45.10	59.05	2
Si	54.90	40.95	
O	41.61	55.68	3
Na	3.92	3.65	
Al	13.42	10.65	
Si	35.11	26.76	
K	5.95	3.26	

Figure 5.2.1.12. EDX result of 20 % sludge added the tile fired at 1100 °C.

EDX analysis conducted on twenty six different areas indicate that average atomic percentage value of Al and Si were 10.02 and 27.2 as given in Table 5.2.1.3. Na, Mg, K and Ca were detected but average atomic percentage values of these elements were less than 5 %.

Table 5.2.1.3. EDX analysis of 20 % sludge added tile fired at 1000 °C in twenty six different areas.

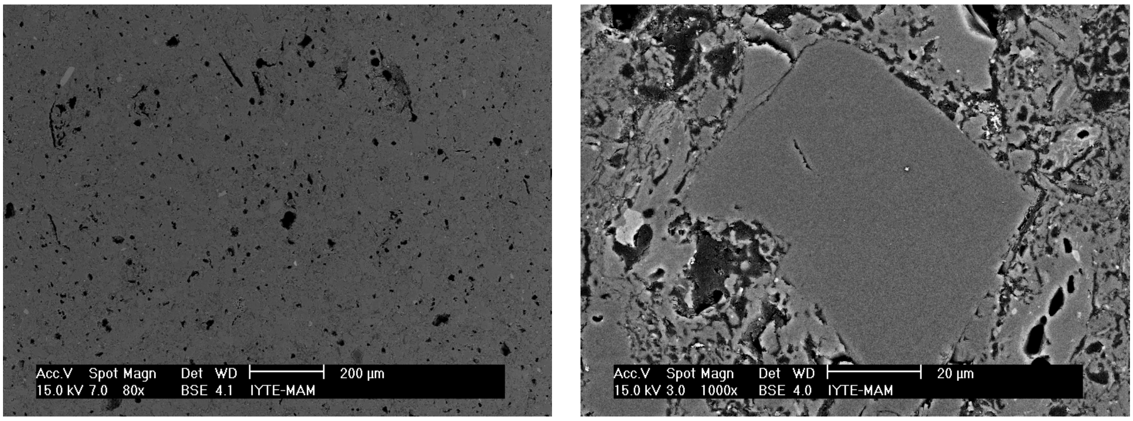
	O	Na	Mg	Al	Si	K	Ca
average	57.6	1.8	0.5	10.2	27.2	1.7	0.8
std-dev	1.4	0.9	0.5	0.8	1.2	0.2	0.8

EDX analysis conducted on eighteen different areas indicates that average atomic percentage value of Al and Si were 10.2 and 28.4 as given in Table 5.2.1.4. Na, K, Fe and Ca were detected but average atomic percentage values of these elements were less than 5 %.

Table 5.2.1.4. EDX analysis of 20 % sludge added tile fired at 1100 °C in eighteen different areas.

	O	Na	Al	Si	K	Fe	Ca
average	56.4	2.3	10.2	28.4	1.8	0.1	0.8
std dev	0.9	0.4	0.9	1.2	0.3	0.4	0.7

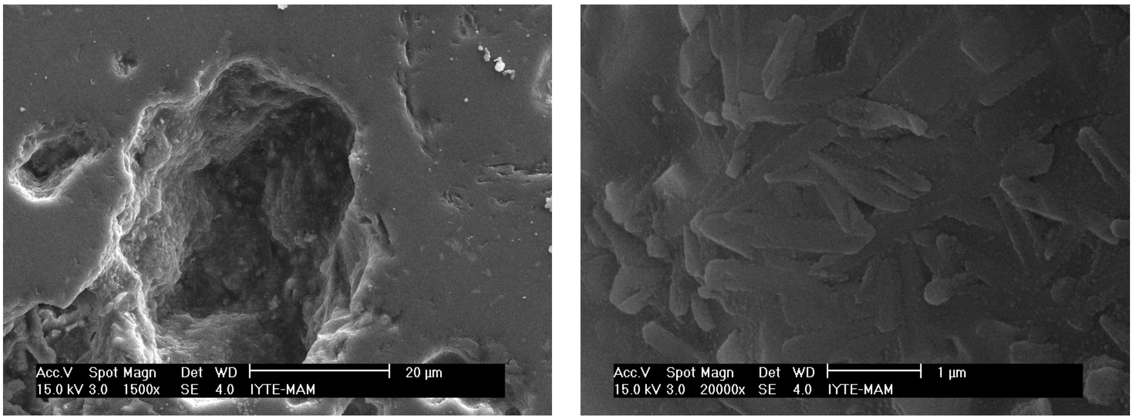
SEM image with BSE mode of the tile containing 50 % sludge additives fired at 1000 °C in Figure 5.2.1.13 shows that there is some porosity in the structure. It seems that firing temperature could be almost enough for sintering.



(a) (b)

Figure 5.2.1.13. SEM images with BSE mode of 50 % sludge added tile fired at 1000°C at (a) 80X and (b) 1000X.

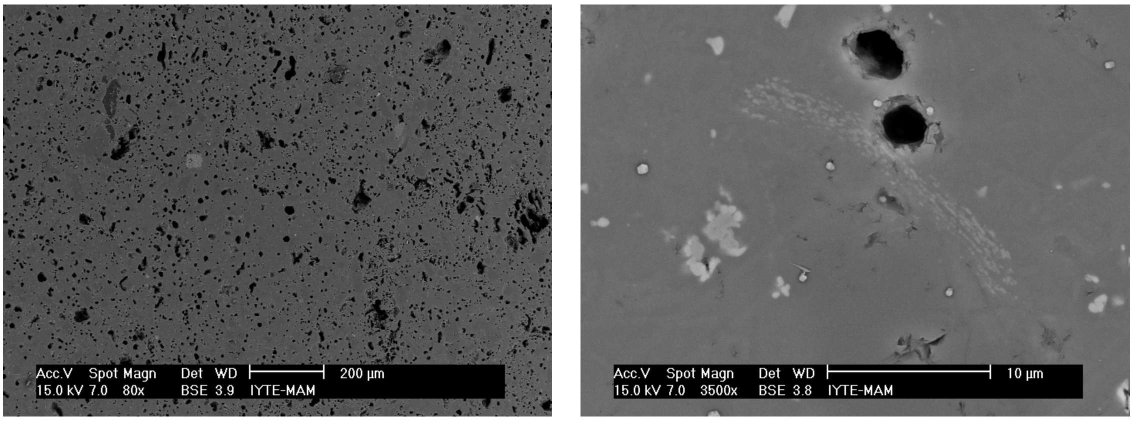
The SEM images given in Figure 5.2.1.14 indicates that pores with diameters of approximately 20 µm were present in the 1100°C sintered pellet. Micron sized grains on the pore walls is visible as seen in Figure 5.2.1.14 b.



(a) (b)

Figure 5.2.1.14. SEM image with SE mode of 50 % sludge added tile fired at 1100 °C at (a) 1500X and (b) 20000X.

SEM image with BSE mode of tile containing 50 % sludge additives fired at 1100 °C given in Figure 5.2.1.15 shows the presence of approximately 4 µm closed pores.



(a) (b)

Figure 5.2.1.15. SEM image with BSE mode of 50 % sludge added tile fired at 1100 °C at (a) 1500X and (b) 20000X.

EDX analysis conducted on twelve different areas indicates that average atomic percentages of Al and Si were 9.41 and 26.16. Zn, K, Ca, Cr, Fe, Cu and Pb were detected but average atomic percentages for these elements were less than 5 % as given in Table 5.2.1.5.

Table 5.2.1.5. EDX analysis of 50 % sludge added tile fired at 1000 °C in twelve different areas.

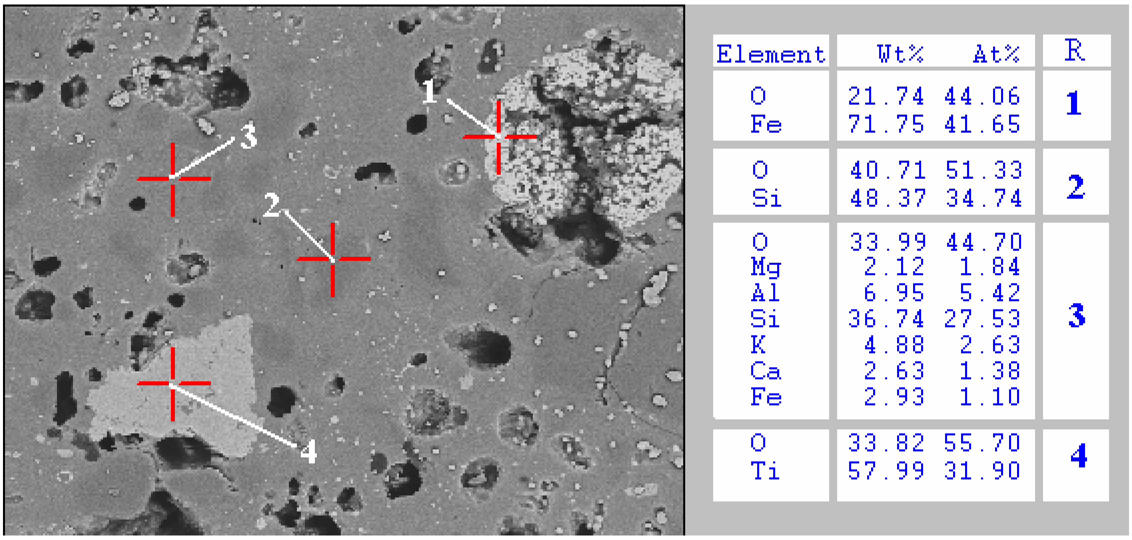
	O	Zn	Al	Si	K	Ca	Cr	Fe	Cu	Pb
average	53,64	1,49	9,41	26,16	1,61	2,61	0,26	1,50	0,60	2,70
std dev	0,65	0,21	0,35	1,27	0,10	0,32	0,10	0,26	0,09	1,66

In EDX analysis of the tile containing 50 % sludge additives fired at 1100 °C, Fe was found in region 1. Si in the form of SiO_2 was observed in region 2. A phase which is rich in Al and Si were mainly determined in region 3 and in region 4 Ti (maybe in form of TiO_2) was detected as given in Figure 5.2.1.16.

Table 5.2.1.6. EDX analysis of 50 % sludge added tile fired at 1100 °C in twelve different areas.

	O	Zn	Al	Si	K	Ca	Cr	Fe	Cu	Pb
average	53,76	1,49	9,31	26,98	1,69	2,58	0,26	1,61	0,49	1,84
std dev	0,68	0,14	0,28	1,58	0,17	0,36	0,12	0,24	0,23	1,60

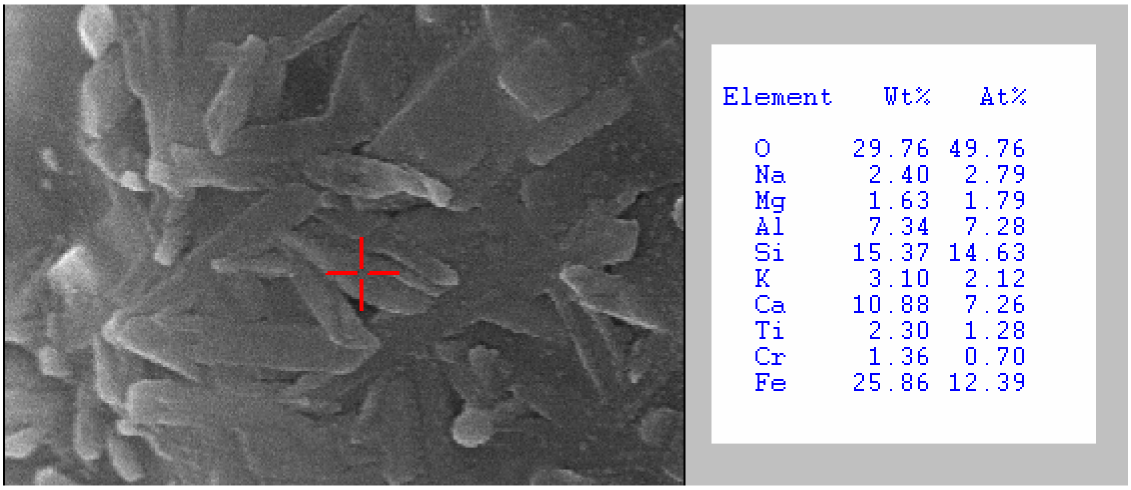
EDX analysis conducted on twelve different areas indicates that average atomic percentages of Al and Si were 9.31 and 26.98. Zn, K, Ca, Cr, Fe, Cu and Pb were detected but average atomic percentages for these elements were less than 5 % as given in Table 5.2.1.6.



Element	Wt%	At%	R
O	21.74	44.06	1
Fe	71.75	41.65	
O	40.71	51.33	2
Si	48.37	34.74	
O	33.99	44.70	3
Mg	2.12	1.84	
Al	6.95	5.42	
Si	36.74	27.53	
K	4.88	2.63	
Ca	2.63	1.38	
Fe	2.93	1.10	
O	33.82	55.70	4
Ti	57.99	31.90	

Figure 5.2.1.16 EDX result of 50 % sludge added tile fired at 1100 °C.

In EDX analysis of tile containing 50 % sludge additives fired at 1100 °C, needle-like crystals was observed and they mainly contained Si, Ca, Al and Fe as seen from Figure 5.2.1.17.



Element	Wt%	At%
O	29.76	49.76
Na	2.40	2.79
Mg	1.63	1.79
Al	7.34	7.28
Si	15.37	14.63
K	3.10	2.12
Ca	10.88	7.26
Ti	2.30	1.28
Cr	1.36	0.70
Fe	25.86	12.39

Figure 5.2.1.17. EDX result of 50 % sludge added tile fired at 1100 °C.

The tile without sludge additives fired at 1000 °C contains quartz and albite (a commonly known feldspar mineral phase with chemical composition of $NaAlSi_3O_8$) phases as seen from the XRD pattern given in Figure 5.2.1.18. The tile containing 50 % sludge additives fired at 1000 °C consists of quartz, hematite (Fe_2O_3) and anorthite ($CaO.Al_2O_3.2SiO_2$) which probably was formed due to the presence of excess amount of calcium in this powder mixture.

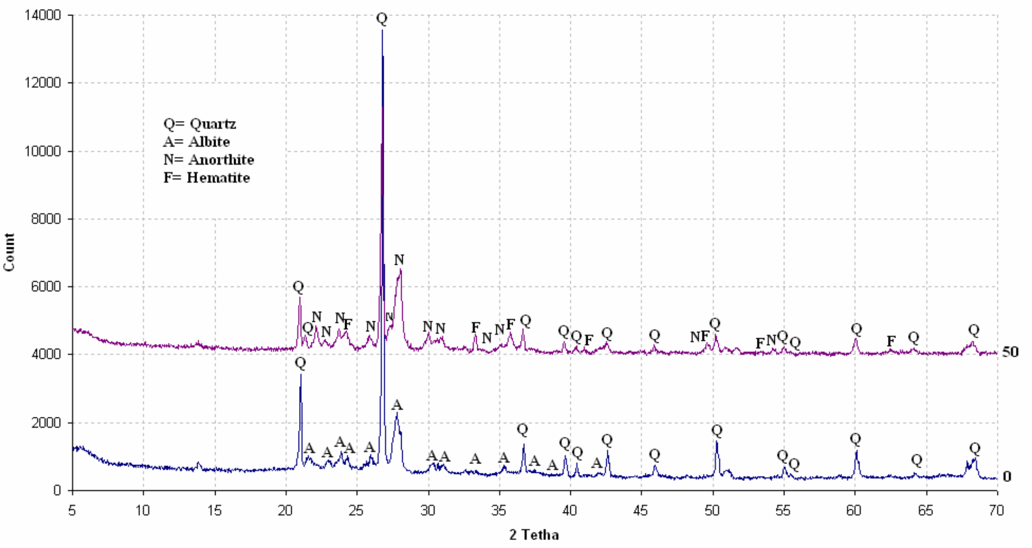


Figure 5.2.1.18. XRD chart of 0 and 50 % sludge added tile fired at 1000 °C.

The tile without sludge additives fired at 1100 °C contains quartz and aluminum silicon oxide as seen from Figure 5.2.1.19. The tile containing 20 % sludge additives fired at 1100 °C consists of quartz, hematite, kyanite and corundum phases. Chemical composition of kyanite is $Al_2O_3.SiO_2$. Kyanite is a silicate mineral which is formed during the regional metamorphism of clay-rich sediments. Kyanite occurs as elongated blades principally in gneisses and schists, and it is often accompanied by garnet, quartz, and mica. There are also peaks showing existence of Al_2O_3 (corundum). Quartz, albite and hematite were the major phases present in the structure of the tile containing 50 % sludge additives fired at 1100 °C as seen from Figure 5.2.1.19.

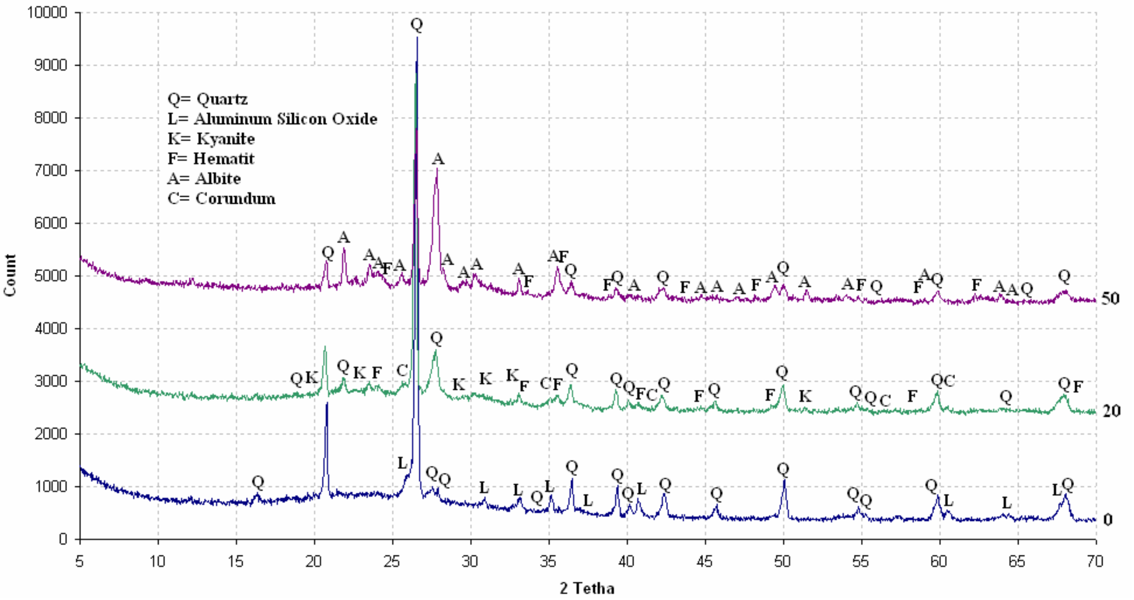


Figure 5.2.1.19. XRD Chart of 0, 20 and 50 % sludge added tile fired at 1100 °C.

Mullite forms as a major phase in the structure of the tiles fired at 1200 °C without sludge additives contains as seen in Figure 5.2.1.20. Mullite formation was not observed in the structure of the tile containing 50 % sludge additives fired at 1200 °C where due to the presence of significant levels of calcium ions anorthite formed in the structure.

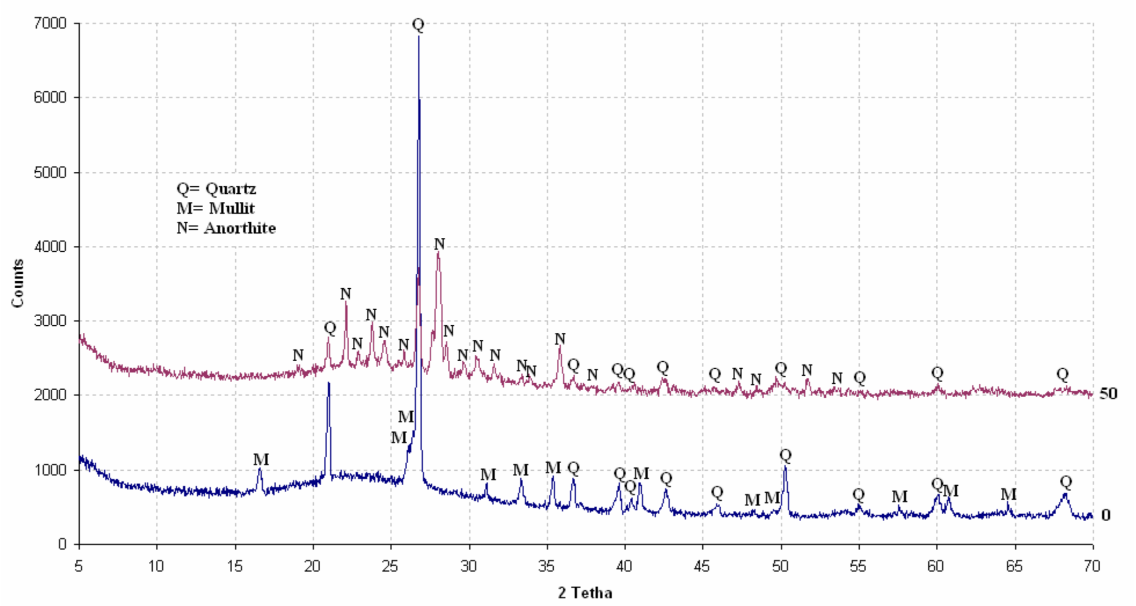


Figure 5.2.1.20. XRD chart of the tile without sludge additives and containing 50 % sludge additives fired at 1200 °C.

5.2.2. Water Absorption, Density Measurement and Firing Shrinkage

Water absorption, density and firing shrinkage are important properties of ceramic products have a great important and they are under very close control in the industry. Water absorption level could be regarded as a significant indication of the level of vitrification/densification and the lower the water absorption the lower the product open porosity. Density also is important to have information about the extent of sintering/densification. In the production of standard size ceramic articles, it is not desired to have a high firing shrinkage which sometimes may depend on the loss on ignition (LOI) of the unfired green structure.

Water absorption was measured by Archimedes Method for all sintered pellets. The water absorption and bulk density of the fired pellets can be determined by this method. The lowest water absorption was determined for the 20-50 % sludge added pellets which were fired at 1100 °C. The water absorption increases with increased sludge content with firing temperature in the 1000-1075 °C range as shown in Figure 5.2.2.1. This behaviour may be related with the calcination of the increasing amounts of calcite with the increase in the sludge addition percent. The porous calcia structure may absorb water which also reacts with the surrounding phases and forming liquid phases to form the new anorthite phase thus decreasing the water absorption through pore closure.

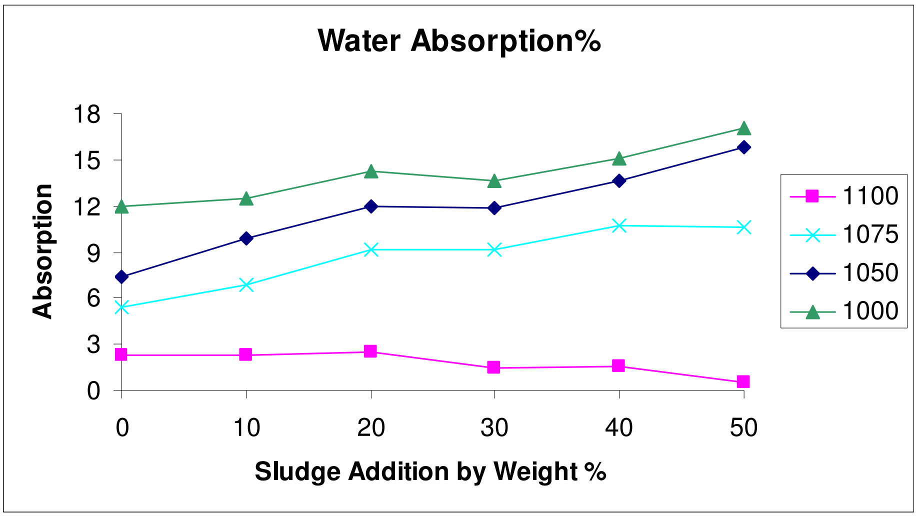


Figure 5.2.2.1. The variation of water absorption with sludge content and sintering temperature.

Green density of the pellets was determined from their dimensions and weight. The pellet which had the highest density was the 30% sludge added pellet as seen in Figure 5.2.2.2.

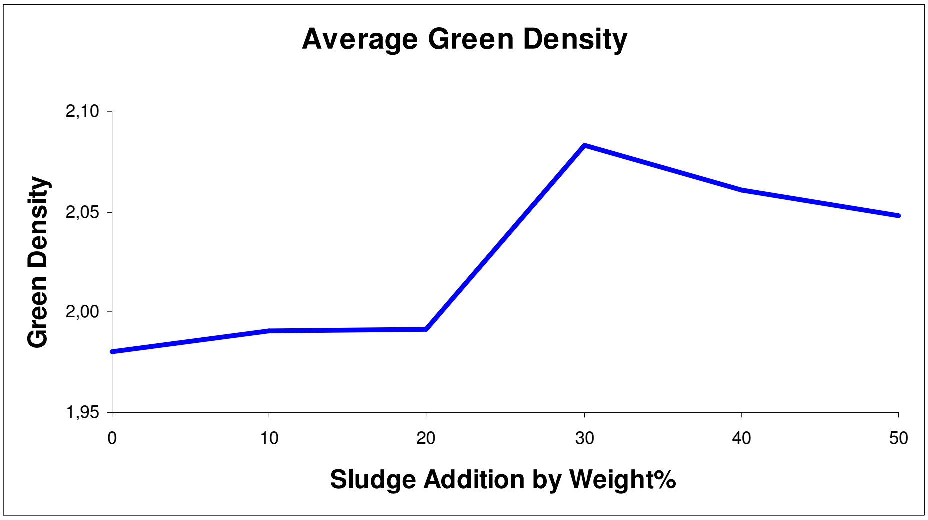


Figure 5.2.2.2. The variation of average green density (g/cm^3) with sludge content.

Bulk densities of the fired pellets were determined and compared by using their dimensions and Archimedes method.

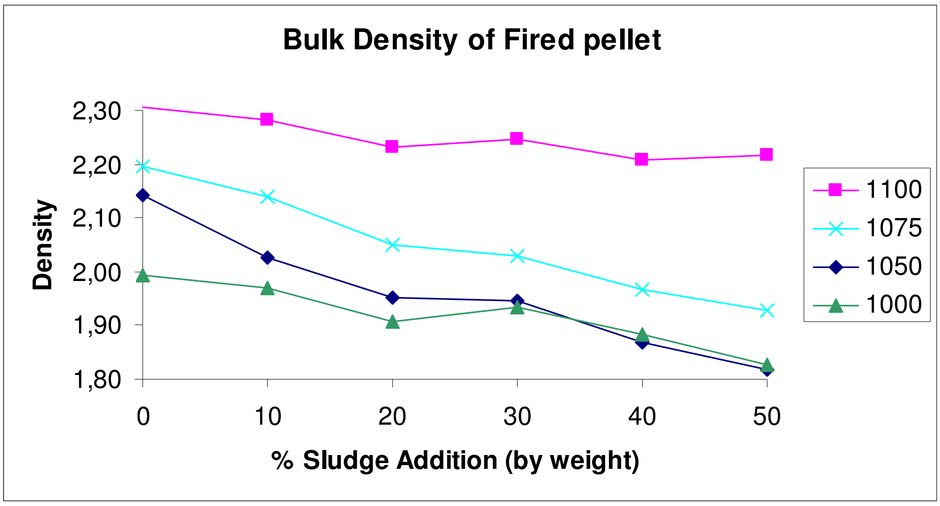


Figure 5.2.2.3. The variation of pellet bulk density determined from pellet dimensions (g/cm^3) with sludge content and sintering temperature.

The bulk densities determined by both methods were very close as seen in Figures 5.2.2.3. and 5.2.2.4. The measurement by Archimedes method has, of course, more accuracy because of the measurement errors of the other method.

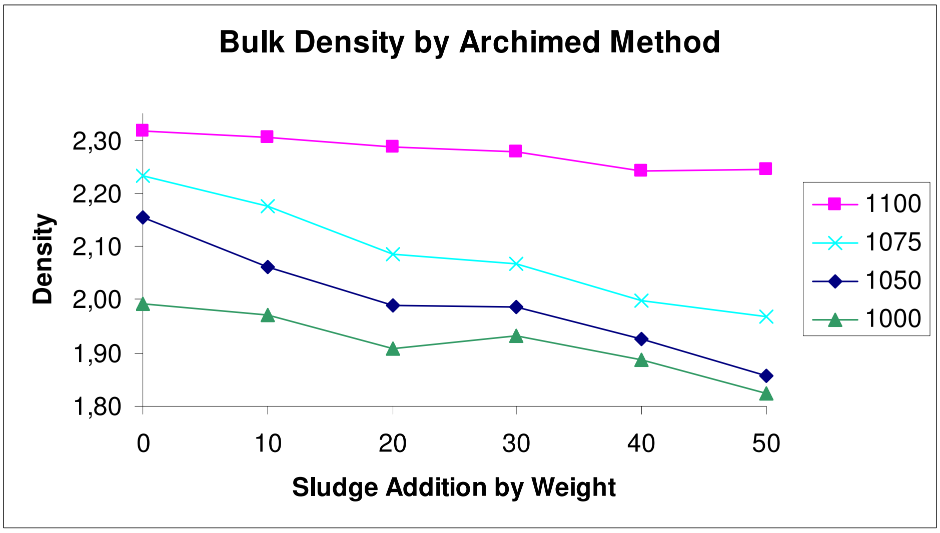


Figure 5.2.2.4. The variation of pellet bulk density determined from Archimedes method with sludge content and sintering temperature (g/cm^3).

Linear firing shrinkage decreases with increasing sludge content up to 1100 °C for all pellets. The linear firing shrinkage varied in the 5-7% range at 1100 °C as shown in Figure 5.2.2.5.

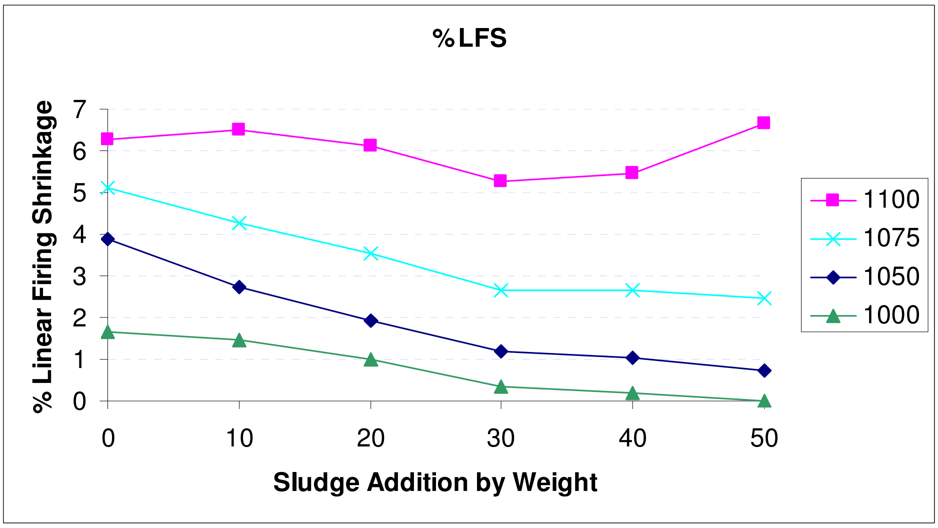


Figure 5.2.2.5. The variation of linear firing shrinkage (LFS) with sludge content and sintering temperature.

The loss on ignition increased with increasing marine sludge addition as given in Figure 5.2.2.6. This was expected because marine sludge contains a significant level of volatile matter such as sulphur, organic compounds etc.

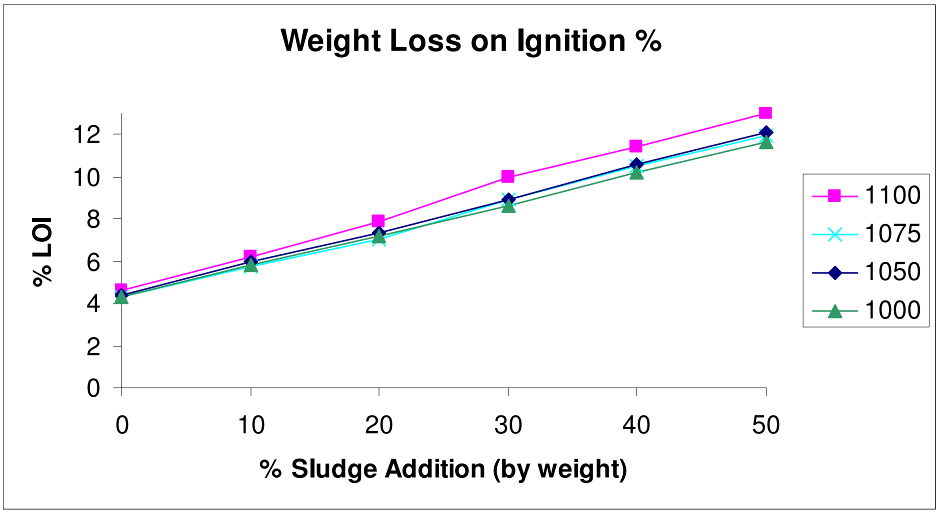


Figure 5.2.2.6. The variation of weight loss on ignition (LOI) with sludge content and sintering temperature.

5.2.3. Leaching Tests

During manufacturing of the enviro-tile a significant amount of marine sludge is incorporated into the tile raw material mixture. Tiles with as much as 20-50 % sludge were fired at 1000 and 1100 °C as given in Table 5.2.3.1. Because of the large amount of marine sludge in the tile amount and behavior of heavy metals in the tile must be closely monitored. These heavy metals must be tied up to the vitrified structure within the tile or else these metals, can be washed out during service which may create health problems.

Table 5.2.3.1. The samples and the corresponding pH levels used in the leaching tests.

S. No	Temperature	Sludge %	pH value
C1	1000	0	4
C2	1000	20	4
C3	1000	50	4
C4	1100	0	4
C5	1100	20	4
C6	1100	50	4
C7	1000	0	9
C8	1000	20	9
C9	1000	50	9
C10	1100	0	9
C11	1100	20	9
C12	1100	50	9

Semi-quantitative analysis results of the C3 sample is given in Table 5.2.3.2. The comparison of semi-quantitative analysis and ICP-MS analysis results indicated that there are extreme differences except for Ca, Cr and Ag. These differences are due to the fact that semi-quantitative analysis yields approximate results. This method was only used for guiding the main body of the leaching tests.

Table 5.2.3.2. Semi-quantitative analysis results of the sample fired at 1000 °C at pH: 4, containing the sludge additives 50%.

Na	Mg	Al	K	Ca	Si	Fe	Cr	Mn	Ni	Cu	Zn	Ag	Pb	Ti	As
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
9.9	0.71	0.43	12	2.4	6.5	0.29	4.1	2.2	12	19	150	2.4	1.9	10	27

The results of the first set of leaching experiments indicated the migration of Mg, Al, K, Ca and Fe in the ppm level where as in the ppb level for Cr, Mn, Co, Ni, Cu, Zn, Ag, Cd and Pb from the tile to the solution as given in Table 5.2.3.3.

Table 5.2.3.3. The results obtained from the first set of leaching tests.

	Unit	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
Mg	mg/l	0.78	3.95	0.85	0.81	2.29	2.01	0.34	4.83	4.65	0.41	1.62	0.28
Al	mg/l	0.73	3.90	0.80	0.76	2.24	1.96	0.29	4.78	4.60	0.37	1.58	0.23
K	mg/l	5.31	3.52	2.95	7.77	3.73	2.62	4.97	4.65	4.00	1.66	2.39	1.60
Ca	mg/l	5.25	7.16	6.85	1.16	3.29	2.60	1.45	7.80	7.08	1.00	1.74	1.12
Fe	mg/l	0.35	1.05	0.28	0.25	0.63	0.59	0.24	0.97	0.97	0.20	0.42	0.20
Cr	µg/l	38.77	27.77	6.55	14.18	7.28	3.82	25.72	15.88	9.74	12.21	5.16	2.71
Mn	µg/l	43.63	32.34	6.54	12.86	9.21	5.83	28.43	18.78	9.53	12.94	5.00	2.07
Co	µg/l	34.91	19.99	1.47	9.61	3.21	0.22	23.28	7.88	1.14	9.41	1.17	0.00
Ni	µg/l	37.51	23.84	6.01	12.39	10.54	5.26	29.52	14.08	7.35	12.06	5.14	4.42
Cu	µg/l	46.26	26.29	3.82	13.84	15.39	9.81	39.20	19.30	11.75	12.47	11.98	7.91
Zn	µg/l	127.61	41.81	20.66	31.71	35.23	22.65	60.19	40.45	30.87	25.53	28.43	22.45
Ag	µg/l	7.08	5.16	1.68	6.17	1.96	2.08	2.56	3.40	1.95	4.14	1.70	2.69
Cd	µg/l	36.12	21.73	4.21	10.93	4.66	1.71	23.41	9.51	3.84	11.25	2.54	1.40
Pb	µg/l	118.10	86.37	18.51	49.43	30.07	16.43	79.35	49.89	22.50	42.38	22.38	14.36

The leachability of chromium decreased with the sludge content as shown in Figure 5.2.3.1. The tiles fired at 1000 °C had higher leachability levels than tiles fired at 1100 °C. The tiles had higher leachability levels in the acidic leaching solutions. It should also be kept in mind that these are in ppb levels and may involve significant errors in the determinations.

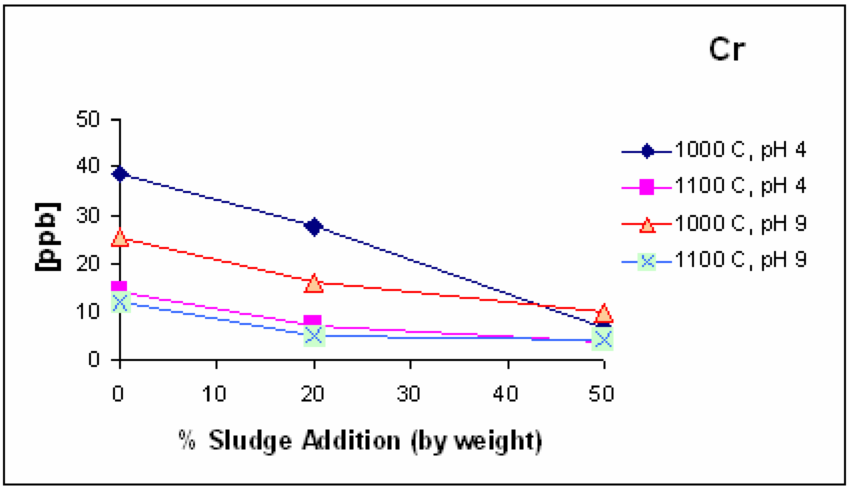


Figure 5.2.3.1. Leachability of chromium in the first set of leaching tests.

The leachability of Pb decreases with sludge content. Tiles fired at 1000 °C had higher Pb leachability values than tiles fired at 1100 °C. The pH=4 solutions had a higher Pb leaching ability than pH=9 solutions as shown in Figure 5.2.3.2.

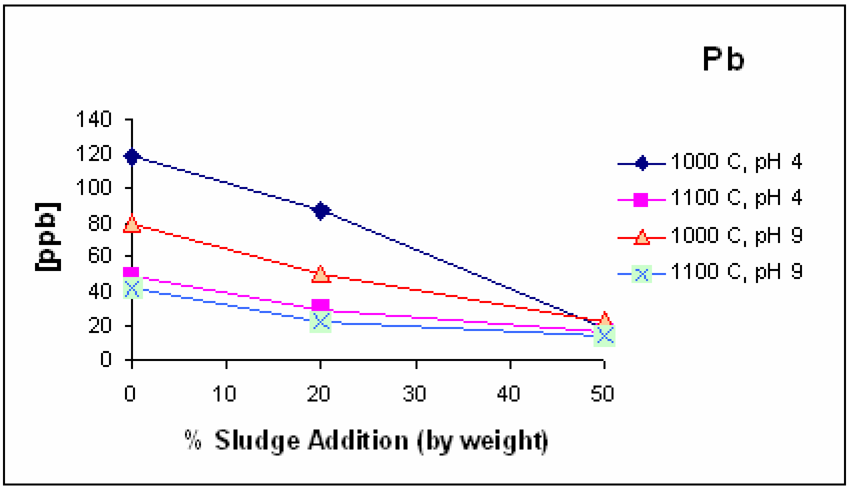


Figure 5.2.3.2. Leachability of lead in the first set of leaching tests.

The leachability of Zn decreases with the sludge content. Tiles fired at 1000 °C had higher Zn leachability values than tiles fired at 1100 °C. The pH=4 solutions had a higher Zn leaching ability than pH=9 solutions as shown in Figure 5.2.3.3. There were almost no differences in Zn leachability between tiles containing 20 % and 50 % sludge additives.

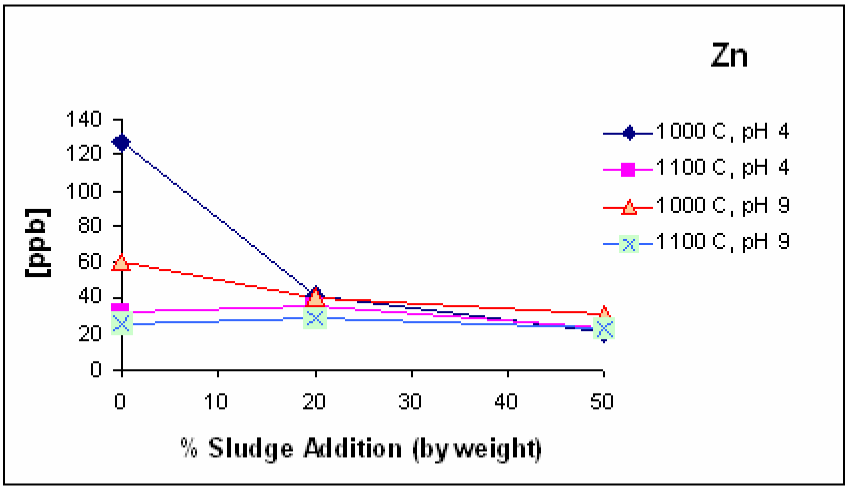


Figure 5.2.3.3. Leachability of zinc in the first set of leaching tests.

The leachability of copper decreased with sludge content. In general, tiles fired at 1000 °C had higher Cu leachability values than tiles fired at 1100 °C. The tiles fired at 1100 °C and leached at pH 4 and pH 9 had slightly higher Cu leachability. The pH=4 solutions had a higher Cu leaching ability than pH=9 solutions as shown in Figure 5.2.3.4.

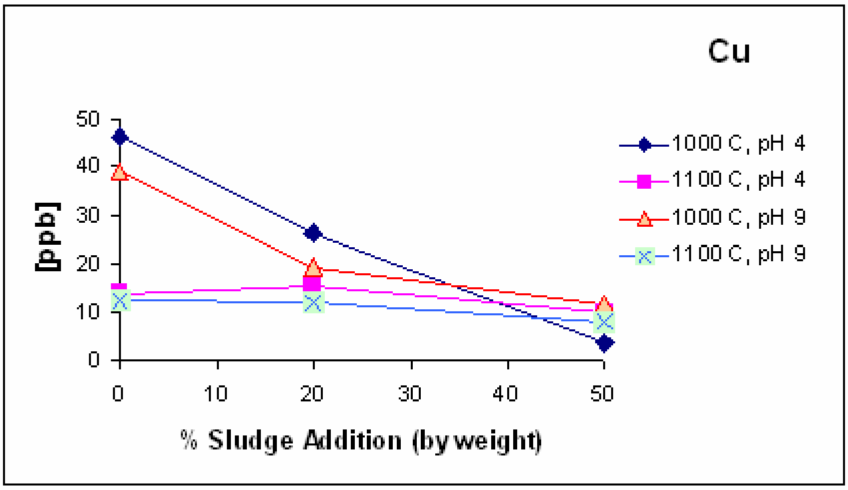


Figure 5.2.3.4. Leachability of copper in the first set of leaching tests.

For second set of leaching experiment, semi-quantitative analysis was applied on one sample, fired at 1100 °C and containing the sludge additives 50% (C12), considered highest heavy concentration to learn approximate concentration as given in Table 5.2.3.4.

Table 5.2.3.4. Semi-quantitative analysis results of the sample C12.

Na	Mg	Al	K	Ca	Si	Fe	Cr	Mn	Co	Ni	Cu	Zn	Ag	Cd	Pb
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppb	ppb	ppb	ppb	ppb	ppb	Ppb	Ppb
6.7	1.38	1.14	3.96	5.4	7.8	0.9	2.58	13.8	0.6	4.74	9.6	84	6.6	0.306	3.3

Semi-quantitative analysis results of the C12 sample is given in Table 5.2.3.4. The comparison of semi-quantitative analysis and ICP-MS analysis results indicated that there are extreme differences except for Fe and Cu. These differences are due to the fact that semi-quantitative analysis yields approximate results. This method was only used for guiding the main body of the leaching tests.

The results of the second set of leaching experiments indicated the migration of Na, Mg, Al, K, Ca and Fe in the ppm level where as in the ppb level for , Mn, Co, Ni, Cu, Zn, Ag, Cd, Ba and Pb from the tile to the solution as given in Table 5.2.3.5.

Table 5.2.3.5. Results of the second set of leaching test test.

		pH 4			**pH 9**		
	Unit	**0**	**20**	**50**	**0**	**20**	**50**
Na	ppm(mg/l)	37.1	96.6	97.3	23.5	40.5	29.5
Mg	ppm(mg/l)	2.3	3.8	6.4	2.1	3.7	5.6
Al	ppm(mg/l)	11.9	5.3	5.6	7.8	7.7	5.7
K	ppm(mg/l)	17.6	14.7	17.6	15.4	13.9	18.4
Ca	ppm(mg/l)	2.8	7.9	13.5	2.3	7.1	10.5
Fe	ppm(mg/l)	1.2	0.6	0.8	0.9	1.0	0.7
Cr	ppb(μg/l)	10.4	5.3	3.7	7.6	11.5	3.1
Mn	ppb(μg/l)	20.2	9.7	19.7	12.5	15.1	12.0
Co	ppb(μg/l)	0.6	0.0	0.2	0.7	1.5	0.6
Ni	ppb(μg/l)	17.4	2.6	2.6	4.1	3.7	3.6
Cu	ppb(μg/l)	29.3	19.6	9.3	12.2	10.0	10.1
Zn	ppb(μg/l)	131.1	205.7	77.3	63.9	178.2	47.7
Ag	ppb(μg/l)	9.6	0.7	3.0	6.2	1.9	0.7
Cd	ppb(μg/l)	0.0	0.0	0.0	0.6	0.5	0.3
Ba	ppb(μg/l)	103.8	56.4	52.6	87.6	62.7	53.8
Pb	ppb(μg/l)	37.0	8.2	2.6	25.2	11.2	2.6

As seen from Figure 5.2.3.5, leachability of chromium decreases with sludge content for tiles leached at pH 4. There was an increase chromium value of the tile containing 20 % additive while there was a decrease chromium value of the sample containing 50 % at pH 9. There were a little difference when first set and second set leaching experiments were compared in Cr although experimental condition was changed.

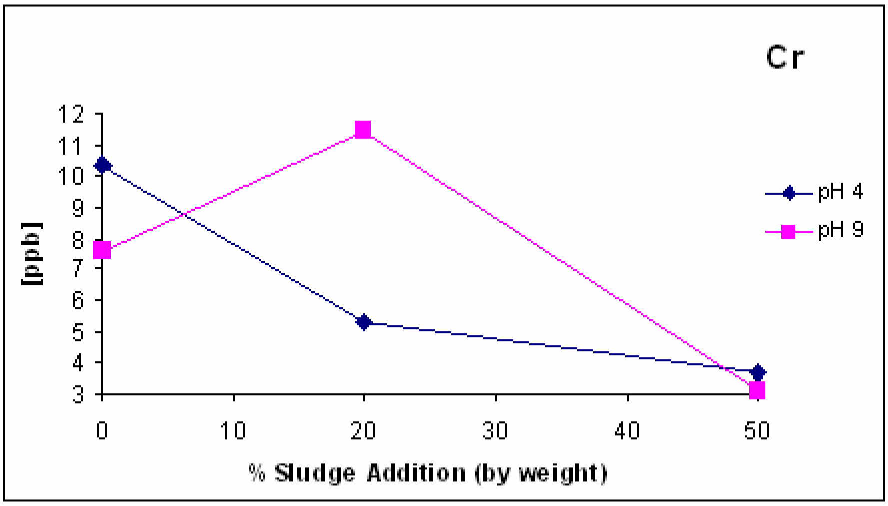


Figure 5.2.3.5. Leachability of chromium in the second set of leaching tests.

Leachability of lead decreases with sludge content. Samples leached in acidic media had less leachability than basic media as seen from Figure 5.2.3.6. When first set and second set leaching experiments were compared, it was determined there were no so much differences between both set leaching experiment.

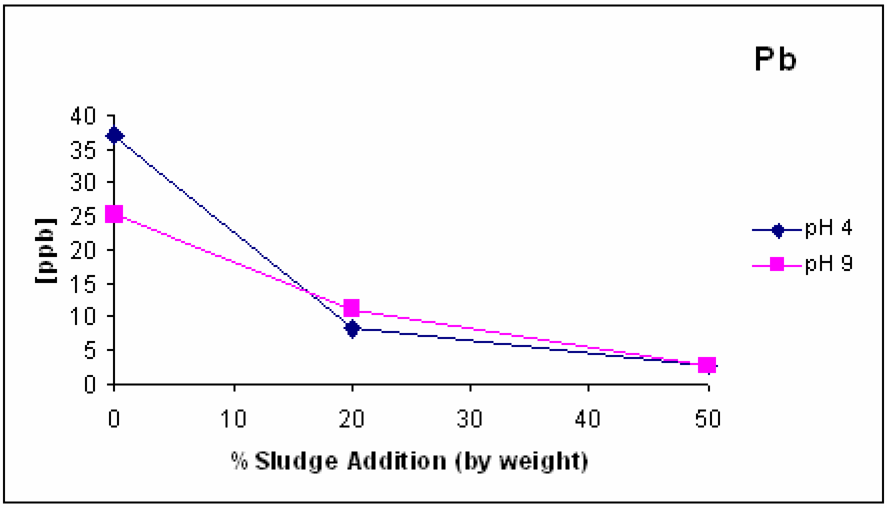


Figure 5.2.3.6. Leachability of lead in the second set of leaching tests.

Leachability of zinc increases with sludge content until the sludge additives were reached 20 % percentage. It decreases as sludge additives increases until the sludge additives were reached 50 %. Tiles leached in acidic media had lower Pb leachability than basic media as seen from Figure 5.2.3.7.

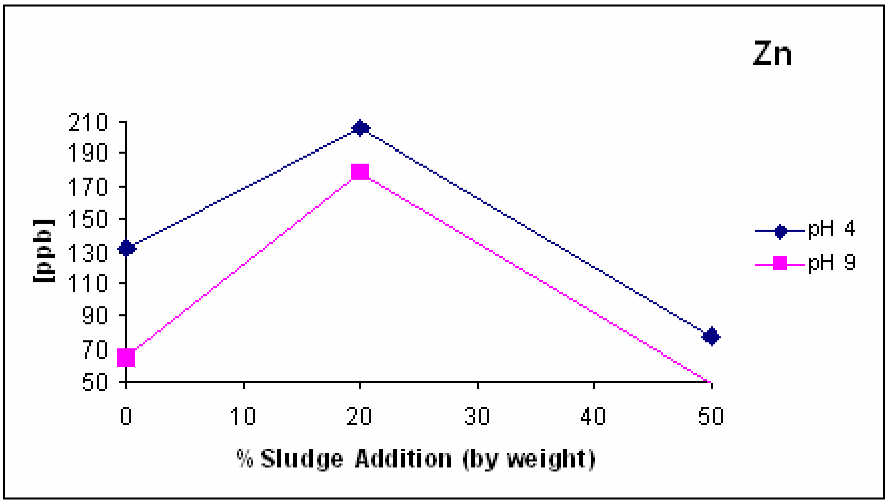


Figure 5.2.3.7. Leachability of zinc in the second set of leaching tests.

Leachability of copper decreases with sludge content. There were increase the tile containing the sludge additives 50 % higher than the tile containing the sludge additives 20 % at pH 9 as given in Figure 5.2.3.8.

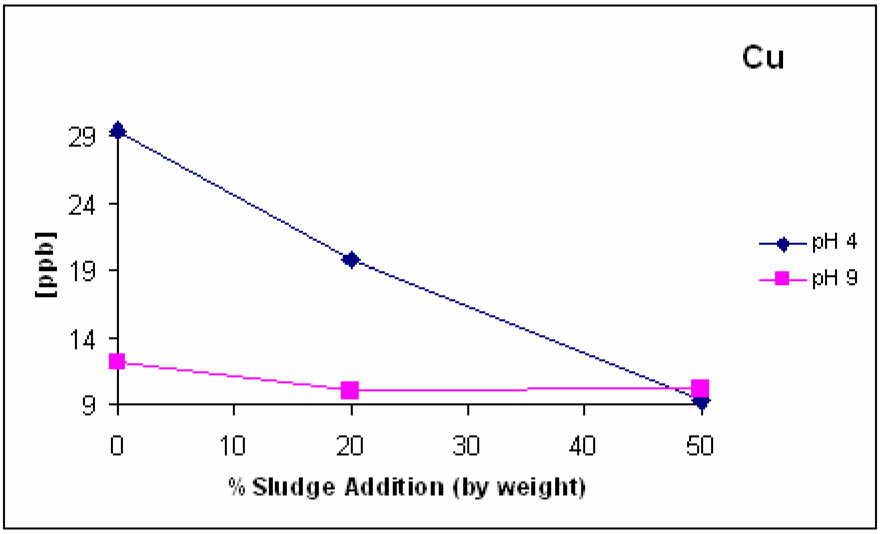


Figure 5.2.3.8. Leachability of copper in the second set of leaching tests.

Leachability of Calcium increases with sludge content. Tiles leached at pH 4 had higher Ca leachability than tiles leached at pH 9 as given in Figure 5.2.3.9.

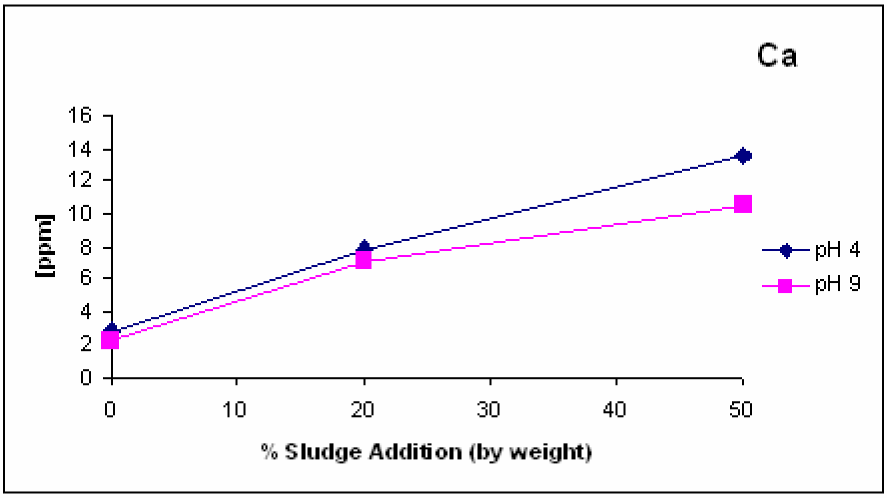


Figure 5.2.3.9. Leachability of calcium in the second set of leaching tests.

Leachability of Magnesium also increases with sludge content. Tiles leached at pH 4 had higher Mg leachability than samples leached at pH 9 as given in Figure 5.2.3.10.

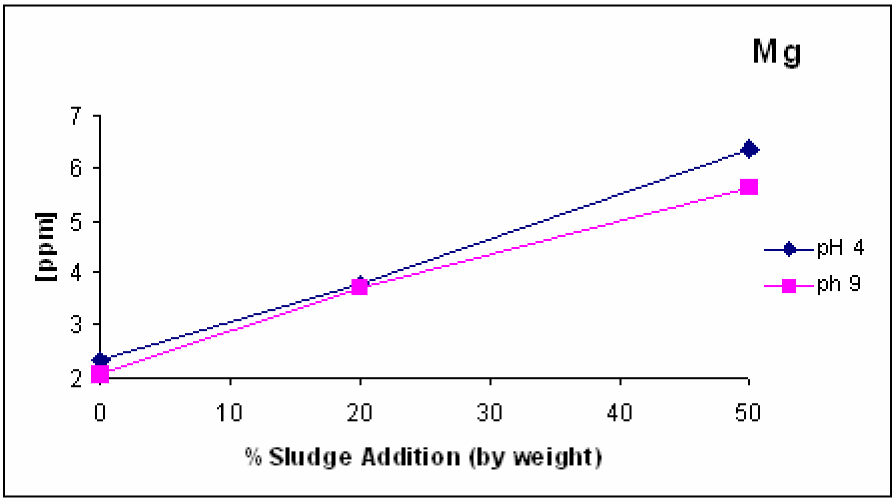


Figure 5.2.3.10. Leachability of Magnesium in the second set of leaching tests.

Leachability of nickel decreases with sludge content. Although there was no so much differences of nickel value at pH 9, firstly a decrease were observed until the sludge additives % 20 then it remained without change at pH 4. Samples leached in acidic media had lower Mg leachability than basic media as seen from Figure 5.2.3.11.

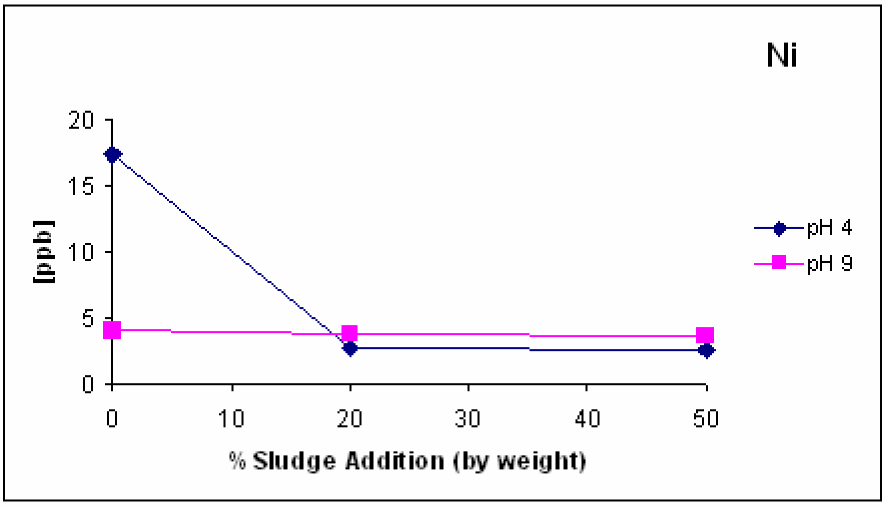


Figure 5.2.3.11. Leachability of nickel in the second set of leaching tests.

Leachability of cadmium decreases with sludge content. Tiles leached in acidic media had lower Cd leachability than basic media as seen from Figure 5.2.3.12. There were no value in the sample containing 20 % and 50 % at pH 4.

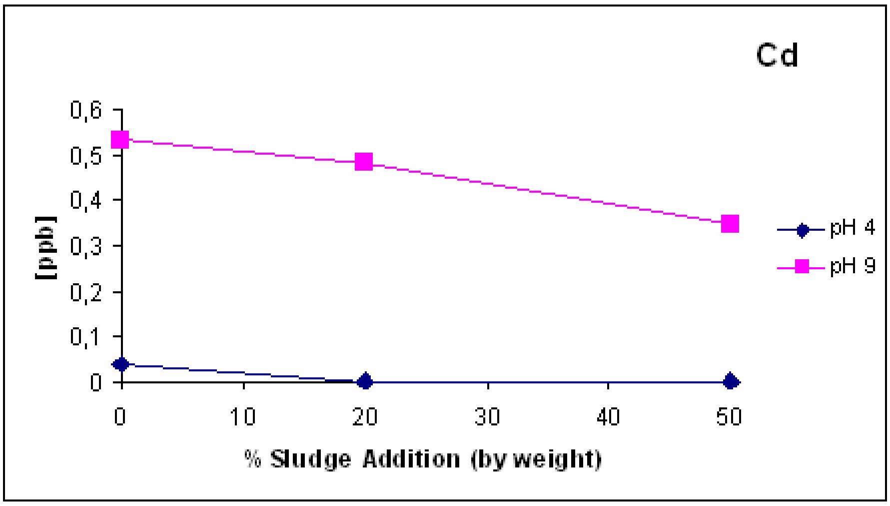


Figure 5.2.3.12. Leachability of cadmium in the second set of leaching tests.

5.2.4. Analysis of Mechanical Properties

Compression testing is very important in view of mechanical behavior measurement technique for ceramic tile production. In first set compression tests, it was applied on the tile pellets, which were pressed with the stainless steel die (diameter:

15mm), marine sludge additives 0, 10, 20, 30, 40 and 50% and fired at 1000, 1050, 1075 and 1200 °C by one replicate.

In second set compression tests, tiles which were marine sludge additives %20 and %50 and without the sludge additives were pressed with the stainless steel die (diameter: 20mm) and fired at 1000, 1050, 1100 °C by three replicates meaning that three samples were prepared for each of them. The height of the tiles which were used for second set compression tests were about 20 mm.

As a result of first set tests, best results were achieved in the pellets containing the sludge additives %20, %50 and fired at 1100 °C as seen from Figure 5.2.4.1.

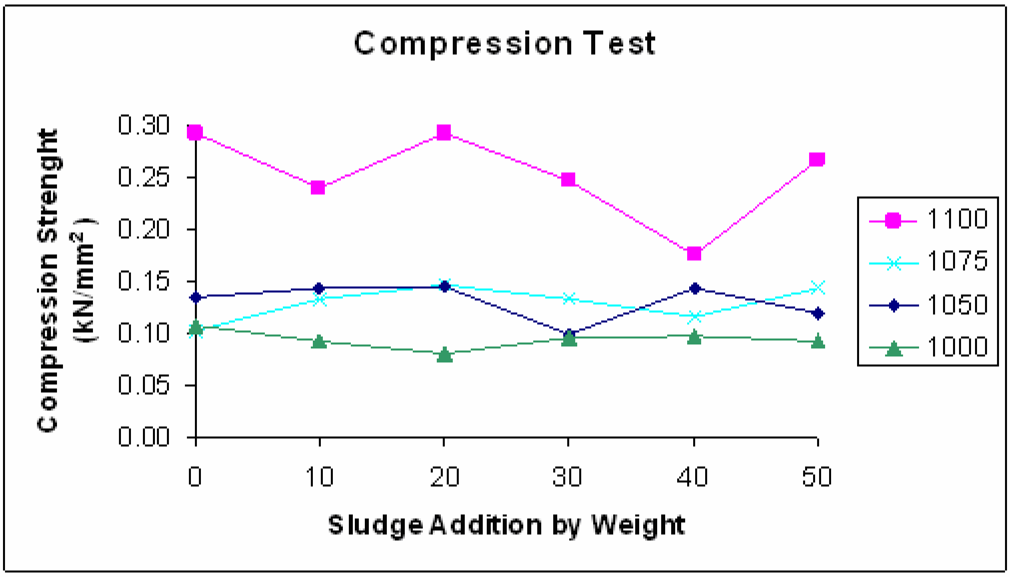


Figure 5.2.4.1. The variation of compressive strength with sludge content for the first set.

As a result of second set tests, best results were achieved in the pellets containing the sludge additives %20, %50 and fired at 1100 °C. Tiles prepared for compression test can be seen in Figure 5.2.4.2.

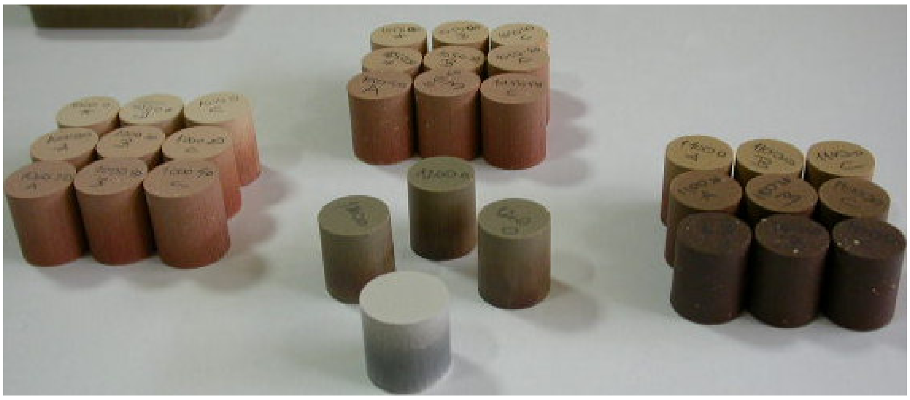


Figure 5.2.4.2. Samples used for second set compression test.

The tile containing 20% sludge additives presented best mechanical properties. In this experiment conditions, some cracks were observed in some samples except for reference sample which was without sludge additives and fired at 1200 °C. Strength decreases as firing temperature increases except for firing temperature of 1100 °C but no samples were reached result of reference sample as seen from Figure 5.2.4.3. It became unavailable to use as ceramic tile due to bloating when samples containing the sludge additives were fired at 1200 °C.

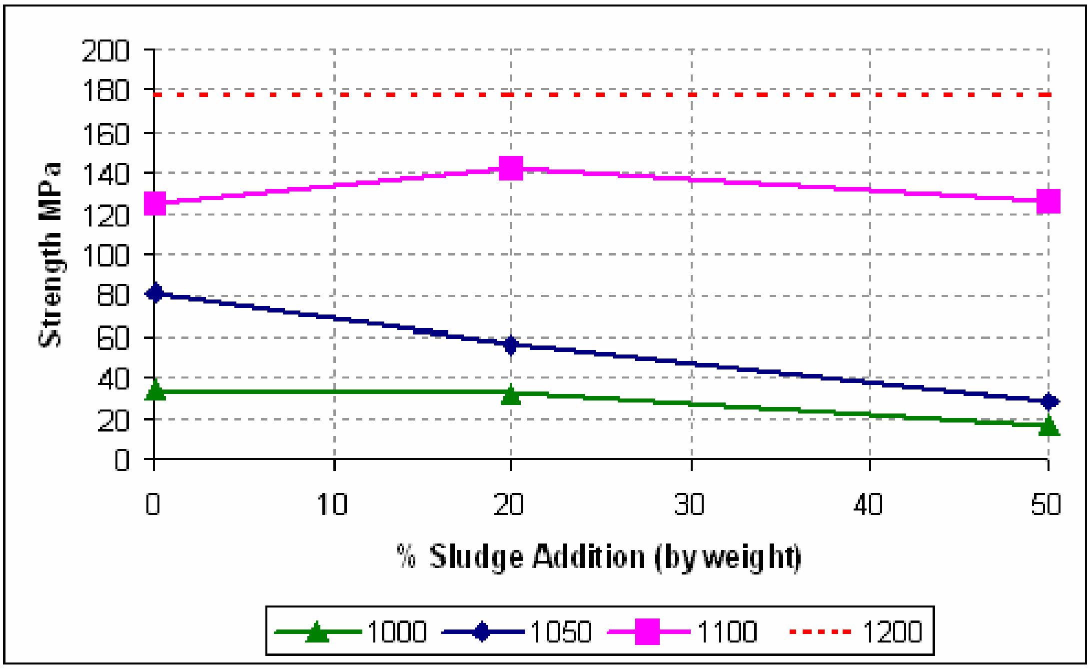


Figure 5.2.4.3. The variation of compressive strength with sludge content for the second set.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Turkey is one of the leading countries in ceramic tile production all around the world. Ceramic tiles containing marine sludge additives up to 50 percent sintered at different temperatures in the 1000-1100 °C range with one-hour firing time were produced and characterized by using different techniques in this thesis.

Marine sludge was pretreated in order to reduce the salt content and to remove excessive shells for further use in the ceramic tile body. The treated marine sludge contains aragonite, illite, quartz, halite and mica phases according to the XRD analysis. Various types of organic compounds were detected in the sludge by the FTIR analysis. Weight loss of treated marine sludge was about 21 % as determined by TGA analysis. Diatom residues were detected in the treated marine sludge powders during SEM examination. EDX analysis was also applied on treated marine sludge. Al and Si, were mainly determined. The Na, Mg, P, S, Ca, Ti and Fe amounts were less than %5 where the elemental mapping study have indicated some nonuniformities of these elements in the powder structure. The firing studies conducted with the treated sludge at 1000, 1050 and 1100 °C indicated the presence of significant density increase at the sintering temperature of 1100 °C. The presence of a porous structure and the formation of fine grains in the pores were observed in the SEM images of the sintered marine sludge. Hg, As, and Pb were detected in some regions of the sintered marine sludge pellets. Shells present in the sludge were characterized and it was determined that shell structure was about 95 % aragonite by weight, which is a calcium carbonate phase.

A higher level of vitrification was observed in the tiles with marine sludge additives at the same firing temperature when compared with the sludge free tiles during the microstructural analysis of the tiles by SEM although there was some remaining porosity. Heavy metals observed in sintered sludge structure were not detected during the EDX analysis. Anorthite phase was detected due to the presence of increasing amounts of calcium carbonate in the structure with increasing marine sludge content. Water absorption values decreased with increasing marine sludge additives at 1100 °C while it increased with increasing sludge additive at other firing temperatures. Density, as expected, decreased with increasing sludge additive at every firing temperature.

Variations in linear firing shrinkage was determined at 1100 °C with sludge content but it decreased with increasing sludge additives at other firing temperatures. Leaching tests have shown that heavy metals were successfully immobilized in the ceramic tile structure. Compression test results indicated that marine sludge added tiles had higher compressive strength at 1100 °C but these strength values were lower than the 1200 °C sludge free tile compressive strength.

The production of ceramic tiles by using marine sludge additives has been succesfully achieved in this work. The results of this work indicated that blending marine sludge in to the ceramic powder mixtures in the 20-50% range was beneficial for tile production with an optimum firing temperature of about 1100 °C. The incorporation of marine sludge with the powder structure during the masse production may yield a finer and more uniform powder particle size distribution. This may permit the preparation of a well-mixed powder with a better control on final particle size distribution. Use of a spray dryer may also provide a granuler raw material for better consolidation during pressing. Precalcination of marine sludge can be beneficial for final tile properties due to lower weight during firing.

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