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Encapsulation of Hazardous Wastes into Agglomerates

by

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INTRODUCTION

The rapidly developing world of high technology carries with it the growing burden of societal responsibility. Just as it benefits man, it also creates many of today's environmental problems.

Annual production of waste has increased significantly in recent years. In the United States, mining waste and coal refuse alone exceed over 360,000 tons daily, in addition to some 23 x 10^9 tons already accumulated.[1] Disposal becomes a growing concern as the rate of waste production accelerates with population growth and technological advancements. The problem is compounded by increasing toxicity of the waste. Complex and toxic chemicals are prevalent in fertilizers, pesticides, electrochemical and mining applications, down to household cleaning solutions. Traditional methods of landfilling no longer provide a simple solution to the mounting waste problem. Significant leaching results from inadequate land disposal practices, leading to soil and groundwater contamination. Furthermore, the availability of land is greatly reduced with the demand for housing and industrial needs accelerating. Another major consideration is the rising cost of disposal which, in most cases, becomes the limiting factor in the selection of an appropriate disposal method.

Assessment of conventional methods of treatment and disposal brings to fore the true nature of the waste problem. It should address both matters of rendering the waste non-hazardous and reducing the waste stream. With the enactment of stringent regulations imposed by legislation, the need for a more specific, safe, and cost-effective technology becomes even more difficult.

In response to the changing pattern of supply and demand of materials and energy, economic factors, and heightened concern for the quality of the environment,[1] utilization of waste materials is highly encouraged. Materials and energy conservation and control of waste and pollutants are among the benefits derived from such . This practice has gained wide acceptance in a variety of industrial and agricultural fields. The construction industry meets this need in transforming large amounts of solid waste into building materials. Waste-derived building composites have in many instances been the technological equivalent of new materials produced from natural resources.[1] Specific applications include the use of fly ash and slag in blended cements, waste glass as a raw material for lightweight aggregates, and even polyethylene and vinyl plastics converted into park benches, wetland walkways, and wildlife signs.

The use of fly ash as partial replacement for cement in concrete has become routine practice in recent years. It has demonstrated excellent performance in the improvement of strength and durability of concrete. Fly ash bearing concretes commonly reach the strengths of reference concrete prepared from the same materials after only several weeks, and often surpassing the strength of plain concretes in a few months. Extra strength gain is achieved at lower cement content, thereby encouraging increased usage of fly ash.

Advances are being directed to finding other areas of utilization for coal combustion byproducts, of which fly ash is a major component. With the current energy shortage, the demand for coal is expected to increase substantially. A major shift to coal-fired power plants has generated over 80 million tons of coal combustion by-products a year.[2] In fact, Iowa alone currently produces over 700,000 tons of fly ash annually and only 25% is being utilized in the construction industry.[3] The remaining 75% is sluiced to disposal ponds or wasted in sanitary landfills. The average cost of disposal easily runs over $10/ton according to Electrical Power and Research Institute (EPRI) estimate. Other utilities report over $50.00/ton due to limitations and restrictions on land disposal.[2] The costs only reflect on-site, unlined facilities and are predicted by EPRI to have a threefold increase in the next decade.

Among other uses of fly ash in concrete production are as cement raw material, blended cement, admixtures, and stabilizing agent in base and road construction. The latest application is in the field of lightweight concrete as synthetic aggregates. Since approximately 80% of the volume of concrete is occupied by the aggregates, it opens a new venue of utilizing large volumes of fly ash. The most common method of manufacturing these aggregates consists of pelletizing fine powders and sintering the green pellets at a temperature of 1100-1200° C.[4] The purpose of sintering is to burn the fuel components inherent in the coal ash. The result is spherical granules with a smooth surface, brick-like appearance and strengths comparable to that of natural aggregates. These synthetic lightweight aggregates are already commercially available but research is still ongoing to improve the performance of the products and increase processing efficiency.

Fly ash is also being used effectively in stabilization and solidification procedures involving a variety of industrial and municipal wastes. It is mixed with waste to reduce liquidity and therefore improve handling characteristics. Usually, fly ash is employed in conjunction with other binders to activate the pozzolanic and self-cementing characteristics required to stabilize and solidify the waste. Several commercial applications incorporate the use of lime or portland cement in treatment of hazardous waste and involve in-situ mixing, stabilization, and final disposal of the wastes. To date, there are three stabilization processes that have been patented namely Stablex Corporation, U. K. Patent No. 1,485,625 ; I. U., Conversion Systems, Inc., U. S. Patent No. 3,785,840; and Velsicol Chemical Corp., U.S. Patent No. 4,615,809.[5] However, the implications of long-term performance of these processes on the environment remain unanswered in the absence of actual long term field data. Predictive modelling based on laboratory bench-scale testing is the basis for potential long-term effects. Hence, actual application in the industrial world remains to be seen.

Clearly, the development of new commercial applications capable of absorbing significant ash quantities is fastly gaining widespread attention. Use of coal ash minimizes waste disposal and reuses the mineral matter contained in the ash itself. Agglomeration of fly ash offers an alternative to disposal and produces granules with strong lightweight aggregate potential. Such innovative utilization of these coal combustion byproducts have been investigated in small scale experiments either for use as aggregates or as storage options during high-peak-supply and low-demand season. Commercial methods have been adopted and the results appear to be economically feasible for field pilot plant production of agglomerated fly ash.[3] Fly ash agglomeration offers granules of wide size distributions which makes them ideal for use as road base or concrete aggregates.

The results of the commercial methods of fly ash agglomeration encourage its use in the field of waste management. Encapsulation of toxic waste by agglomeration takes full advantage of the inherent pozzolanic and cementitious properties of fly ash in stabilizing toxic waste. Significant leaching is reduced by encasement in a low porosity, solid matrix of high structural integrity. Chemical fixation appears to be viable through partial subsitution of elements or compounds in the hydration of high calcium fly ash. The cost of treatment and disposal is minimized, with a strong possibility on utilization by the construction industry.

OBJECTIVES AND SCOPE OF THE STUDY

The objective of this study was to investigate the feasibility of using the cementitious properties and agglomeration characteristics of coal conversion byproducts to encapsulate and immobilize hazardous waste materials. The intention was to establish an economical way of co-utilization and co-disposal of wastes. In addition, it may aid in the eradication of air pollution problems associated with the fine-powdery nature of fly ash.

Encapsulation into agglomerates is a novel approach of treating toxic waste. Although encapsulation itself is not a new concept, existing methods employ high-cost resins that render them economically unfeasible. In this investigation, the toxic waste was contained in a concrete-like matrix whereby fly ash and other cementitious waste materials were utilized. The method incorporates the principles of solidification, stabilization and agglomeration.

Another aspect of the study is the evaluation of the agglomerates as possible lightweight aggregates. Since fly ash is commercially used as an aggregate, it would be interesting to study the effect of incorporating toxic wastes in the strength development of the granules.

In this investigation, the fly ash self-cementation process was applied to electroplating sludges as the toxic waste. The process hoped to provide a basis for delisting of the waste as hazardous and, thereby greatly minimize the cost of its disposal. Owing to the stringent regulatory requirements for hauling and disposal of hazardous waste, the cost of disposal is significant. The current practice for disposal is solidifying the waste with portland cement and dumping the hardened material in the landfill where the cost varies between $700- 950/ton. Partially replacing portland cement with fly ash in concrete has proven beneficial, therefore applying the same principles in the treatment of toxic waste looked very promising.

The effect of using cement kiln dust in the fly ash agglomeration of a metal-rich sludge was also investigated. Its stabilization and solidification potential in the fixation of heavy metals were analyzed together with high calcium fly ash, as well as its contribution to the development of strength of the agglomerates. Literature has indicated its excellent solidification capacity but its application in the field of agglomeration has been limited. This investigation then hoped to initiate future research on the long term effect of using kiln dust and high calcium fly ash in the agglomeration/encapsulation of heavy metals.

REVIEW OF LITERATURE

Agglomeration

Agglomeration is a general term customarily used to describe any aggregation of small particles, either in dry form or in solution. In this work, it is referred to as a size enlargement operation used to improve the usefulness of fine materials. All throughout the text, it will be used synonymously with granulation. It should, however, be differentiated with pelletization which also refers to a method of granulation. Pelletization is basically the formation of green balls, afterwhich they are dried, pre-heated, and fired to a temperature of 2280-2460°F while maintaining oxidizing condition.[6] Subsequent cooling of sintered pellets follows. Green pellets indicate unfired or unsintered granules and will be then defined as such.

Agglomeration was originally developed for the steel industry in up-grading the quality of fine coals and ores. Very fine magnetite concentrates were wasted since they did not make ideal blast-furnace feed. Using them only result in high fuel consumption. The introduction of the granulation process provided a homogenous, spherical feed for the blast furnace and improved fuel efficiency by 50%. The pelletization process has since been extended to treatment of low-grade ores and in making blended ore pellets from lime and silica, and, as such, is regarded as a vital step in the manufacture of high quality ores.[6]

The benefits derived from agglomeration by the steel industry paved the way for its use on a much wider scale, from pharmaceuticals to bulk fertilizers, sintering of ceramic bodies, flocculation of suspended material for mineral separation and water purification.[6] The latest addition is in the field of waste treatment and disposal. Agglomeration of the deleterious substance prevents primary pollution and promotes easier handling and control for disposal of the waste. It has also become a tool for recycling and reutilization of waste materials. The agglomeration of coal combustion byproducts, specifically fly ash, presents a case in point. Thus, the otherwise troublesome waste material is converted into a useful resource and product, coupled with some financial gains.

Physical concepts

Agglomeration is a growth process based on adhesion between particles. The attraction between particles is governed by the nature of the bonding forces acting in the system. Consequently, the physical and chemical properties developed by the agglomerates are greatly enhanced by the forces holding the particles together. Important characteristics like porosity, compressive strength and chemical durability of the granules are strongly influenced by those of the parent materials. Some of these characteristics are particle size and gradation, surface charge, crystal structure, the proximity of particles, the amount of additives, and chemical reactivity of the material.[8] Understanding the interaction between dispersed particles is the key to interpreting the growth mechanisms of agglomeration.

There are two types of bonding forces responsible for the formation of agglomerates, namely the natural (physical) and applied (mechanical) forces.[8,9] The natural forces consist of a) solid bridges formed by sintering, melting and products of chemical reactions, b) adhesional and cohesional forces that are not freely movable in bonding bridges, c) molecular, magnetic, and electrostatic forces, d) interlocking effects due to fibrous and bulky materials, and e) interfacial forces and capillary pressure in movable liquid surfaces. A detailed discussion of these forces is given by Rumpf.[9]

In a system where a binder is essential for agglomeration, the major contributing force is that of the capillary attraction between particles.[8] Interfacial tension exists in the air-liquid boundary, depending on the relative distribution of the air and liquid phases in the porous agglomerate.[8,9,10] In the initial stage of agglomeration where the volume of liquid is relatively low compared to that of the void space, the liquid is described to be in the pendular state.

Liquid held in discrete lens-like rings can be observed at the point of contact and strength is derived from the capillary attraction and the surface tension of the liquid. The latter is responsible for holding the particles together. As the amount of liquid increases, a continuous network is formed from joining of liquid rings. The air is trapped inside the enveloping liquid and the agglomerate is in a funicular state. Lastly, as the moving liquid displaces the entrapped air and completely fills the void spaces, the agglomerate is said to be in a capillary state.

Usually, imparting a rolling, cascading action to the moist material by the use of suitable equipment is adopted to cause the particles to collide and agglomerate. The application of mechanical force has twofold advantages - initiating growth of physical forces and compaction of the particles together. Compaction can only be beneficial if it does not result in breakage of the granules, otherwise, too much mechanical force is being used. The use of balling or agitating device introduces other variables that certainly affects the properties of the final agglomerates. Some of these variables are the geometry, size, and speed of rotation of the balling equipment, feed charge rate, residence time and amount of binder or additives used.[11,12,13,14,15] These variables will be discussed at length under mechanisms of agglomeration.

The different bonding forces existing in agglomeration are commonly referred to as mechanisms of adhesion.[16] They are clearly the products of the physical and chemical processes of interaction of atomic particles of matter. The relationship of different agglomeration variables were explained by Rumpf through the theories of quantum physics. He formulated mathematical expressions in trying to understand the phenomenon of adhesion and, at the same time, the deformation properties and behavior of the agglomerates. However, due to the vast and constant variations introduced in the agglomeration process, an accurate and full quantitative description of the bonding process becomes very tedious.

The bonding process continues to be a phenomenon in a minute and microscopic system. The task of analyzing the growth patterns of agglomeration becomes very difficult, especially in terms of the bonding forces in a particulate system. A common approach is referring to the growth mechanisms of the agglomeration process in order to understand the prevailing physical and mechanical forces.

Mechanisms of agglomerate growth

Extensive studies have been conducted regarding the formation of agglomerates or green pellets by various investigators.[8,10,17,18,19] As a result, different interpretations of the growth processes have been proposed. It is the intention of the writer to familiarize the readers with the basic mechanisms that are relevant to this investigation.

Most of the methods used in agglomeration involves the use of a liquid or a wetting agent to initiate growth of the granules. The most common liquid used is water owing to its high surface tension. As the fine powders get wet, a film of water that is concave toward the air side is evident on the surface. These water-surrounded particles then serve as the nuclei for granule formation. Growth is initiated by collision and subsequent coalescence of the moist particles. This phenomenon is known as nucleation. The intergranular capillary binding force disappears as soon as the liquid completely envelops the solid particles. However, they are held together by the surface tension of the the liquid. The tendency of a water droplet to coalesce is utilized in effecting granule formation by dispersing liquid-solid suspension into droplets.

Subsequent growth of the nuclei can be accomplished by the mechanism of coalescence. Two granules collide and stick together, after which application of mechanical forces, like the tumbling action in the disc, kneads the twin particles into a single, roughly spherical granule.

The granule can still continue to grow in a number of ways. Breakage of the smallest and weakest granules occurs upon collision with the larger ones. This is in continuity with the fact that the crushing strength of a granule is proportional to the square of the diameter, all things being equal. Then the daughter fragments redistribute themselves onto the unbroken ones causing the so-called layering. However, there are unresolved controversies as to the size of the broken fragments. Capes and Danckwerts suggested that fine particles are produced upon collision, followed by the redistribution of their substance in a uniform layer over the larger unbroken granules.[17] On the other hand, Sastry and Fuerstenau countered that the breakage results in a limited number of fragments of finite size.[8] Both of them are actually right, since the size of broken fragments is more a function of the intensity of agitation and the durability of the granules in collision.

Another form of layering also contributes to further enlargement of the granules. Abrasion transfer involves the transfer of an infinitesimal mass from one agglomerate to another. As the granules brushed each other, the abraded particles tend to adhere to the surface of the other one.

In cases where additional moist feed are continuously charged into the systems, there is a corresponding additional mechanism involved. Another form of layering, commonly referred to as snowballing, occurs. The moist feed or the recycled undersize material being added act as nuclei. The fine feed particles form stronger bonds with the larger granules and would be expected to simply layer onto the surface of the established agglomerates rather than to coalesce with other fine particles.

Kaper and Fuerstenau have summarized the growth of agglomerates in a batch process as occuring in three stages: nuclei formation, the transition period, and the ball growth period.[20] Basically, these growth patterns are analogous to the mechanisms previously discussed. Maximum rate of growth occurs during the transition period where coalescence of small, wetted granules predominate. Further agglomeration is effected through abrasion transfer and layering of the granules during the ball growth period.

The different mechanisms can occur simultaneously in a system but one will predominate. It should be noted that the role of water in the agglomeration process is very important, in that the relative occurrence of the various mechanisms is controlled by the amount of moisture and the relative distribution of moisture in an agglomerate.[8] There is a critical moisture range within which strong agglomerates are formed. Sufficient residence time is also essential in determining the ultimate size of the granule.

Methods of agglomeration

Generally, agglomeration can be classified into two types : those with binders and those that are binderless.[21] Binderless agglomeration comprises all size enlargement processes applying high compaction forces and using one or more of the binding mechanisms such as solid bridges, adsorption layers, molecular, electrostatic and magnetic forces, and interlocking bonds. There are also some materials containing natural binders like bituminous components in many coals. On the other hand, there are many types of materials that do not exhibit inherent binding tendencies. Binders are usually added to enforce the adhesion of the solid particles. The main binding mechanisms for such cases are capillary forces, bridges of highly viscous media and freely movable liquid bridges. To enhance the bonding forces, subsequent drying, firing or curing is essential.

There are two common techniques of agglomeration using binders: granulation and pressure compaction. Both methods employ mechanical devices to agitate a bed of moist particles and ensure efficient bonding. The discussion of these two methods provides an understanding of the basic principles and application which is essential in establishing the framework of the agglomeration process adopted in the study. Pressure compaction will be considered first because it illustrates certain basic principles useful in the discussion of the granulation procedure.

Pressure compaction The basic principle of this agglomeration procedure is the application of a relatively low force to bulk materials with sufficient binding tendency or with the inclusion of binders. The fine particles are forced through open holes or dies of different shapes and later cured to obtain sufficient strength. Examples of the equipment used are extrusion press, screw extruder, roll pelleting machine, and gear type pelleting machine. Pellets and briquettes formed this way are cylindrical with a predetermined diameter but variable length.

Compaction of the granules gives the benefits of increasing density to a maximum and reducing porosity to a minimum.[22] This is accomplished through rearrangement of the particles and subsequent filling of the large void spaces. A closer packing of the materials eventually led to plastic flow and fragmentation in order to fill the smaller voids. This process continues until the true density of the material is achieved.

Granulation The process of size enlargement through granulation is a combination of compaction pressure and agitation of the bulk materials. Dry charge of feed is mixed within the granulator and the appropriate amount of liquid is sequentially added in the mix. The cascading, rolling action promotes mixing and agglomeration of the fine particles. It is believed that capillary attraction and molecular adhesion between closely jammed particles are responsible for holding the particles together. The strength of the pellets is developed by compaction as they roll down the sides of the drums or disks. The force of gravity acting through one of the larger spherical bodies applies a tremendous pressure on a small particle at its point of contact with the body or on the particles at the surface of the spherical body itself.[22] A high frictional drag is maintained by keeping the walls of the granulator slightly rough. The interaction of both the gravitational and frictional forces provides a good rolling action and continuous growth of the pellets. The equipment commonly used includes balling drums, cones, and disks depending on the purpose of agglomeration, process complexity, costs and energy consumption.

In the following discussion, the writer will explain the mechanics of pan granulation, the method of agglomeration adopted in this investigation. The factors affecting the production of good granules will be correlated with the method of choice.

Pan granulation The pan granulator is also known as the balling disc or disc granulator and consists essentially of a disc fitted with a peripheral wall.[22] A schematic diagram of a laboratory-scale arrangement is shown in Figure 1. A variable speed motor and drive mechanism is attached to the disc which is inclined to the horizontal. The feed is charged through a separate facility while moisture is added in the form of fine sprays. Scrapers which are attached on the side walls, control the flow of materials and prevent the build-up of materials on the disc. The disc continues to rotate in a clockwise pattern and granules of desired size are gravity discharged over the rim of the pan.

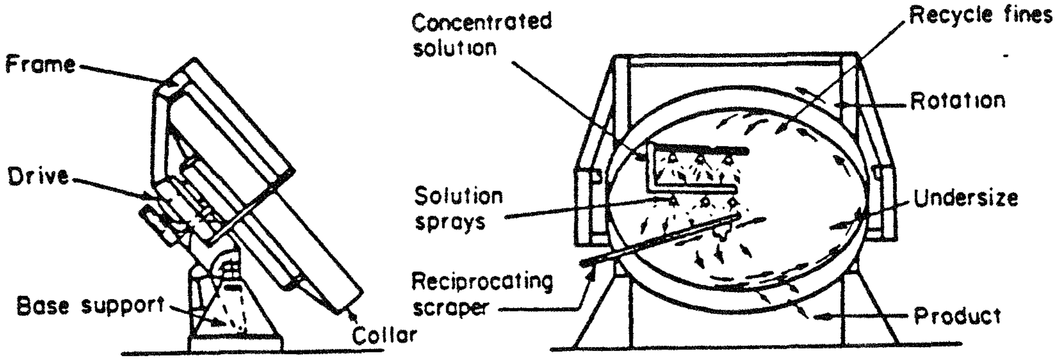


Figure 1. Pan granulator [23]

In a study of the mechanics of balling on disc, the importance of the operating conditions of the disc can not be overemphasized. Major variables include the retention time which is a function of the slope and the feed rate, speed of revolution of the granulator, the preparation of the feed material, and the overall design of the agglomerating machine such as disc diameter and height of the peripheral wall.[11,22] Successful agglomeration can only be achieved through operating at the optimum conditions of the disc. The optimum values vary per machine and on the properties of the feed materials.

The residence time of a given granulator changes with a given feed rate and slope. There is a specific residence time for any given material to form pellets of the desired size The amount of the material present in the disc depends on its feed rate and the holding capacity of the granulator. A faster rate increases the buildup of material in the disc and reduces balling efficiency. It also shortens the retention time of the granules. Solving this problem by increasing the height of the peripheral wall is usually resorted to. However, there is a limit to the depth of the disc in producing good pellets. Beyond this, the rolling capability of the granules is hindered and the total output decreases. Another factor that can also shorten residence time is steep slope of the disc where poor tumbling and agglomeration of materials are effected.

A pronounced effect of the angle of inclination is in the strength developed by the granules as they cascade down the walls of the disc. The compaction of the pellets is greatly reduced as the slope increases and gives the combined effect of minimum balling action in the disc.

The speed of the machine must be adjusted to promote the continuous growth of the pellets. Excessive speed at which the disc is rotated reduces the balling efficiency and causes breakage of the granules. The rolling and cascading action must be gentle enough to allow further layering of the granules.

The disc offers flexibility in operation in that the position of feed addition and water sprays can be modified. The feed can be charged directly under the water sprays to encourage nucleation and ball growth. The water spray can likewise be positioned to promote uniform distribution of moisture in the pellets and layering. The moisture content of the agglomerate is therefore very critical and must be closely regulated to produce a steady flow of good quality. and closely sized green pellets.[22]

Properties of agglomerates and tests

Successful agglomeration is evaluated through the quality of the green pellets. Depending on the usage of the agglomerates, the properties required to qualify for good agglomerates can vary in wide limits. In this case, agglomeration is performed as a means of stabilization of waste with the possibility of using them as synthetic lightweight aggregates. Therefore, the green pellets should possess the qualities of good and sound aggregates. Among the important qualifications relevant to the study are compressive strength, abrasion resistance, weathering resistance, porosity, specific gravity and absorption, and leaching potential. The first three properties generally fall under strength or durability classification.

Strength

General requirements for good quality agglomerates include sufficient strength for handling, transportation, and outside storage. The strength or durability of the green pellets can be measured in terms of crushing strength, abrasion and weathering resistance. The results of the tests would indicate the ability to withstand the rigours of the handling and processing involved.

Evaluation of the crushing strength usually involves breaking the agglomerate between flat, parallel plates in which the lower plate is the pan of balance registering the loads of failure.[6,9,24,25] A common machine used is the Instron machine where more than one granule should be tested in order to give a meaningful statistical reading. The variability, introduced by granule structure and homogeneity, should be accounted for by including the standard deviation in the report of the average crushing strength values. A common problem in this technique is inaccurate determination of the fracture force. The fracture originates from a small primary crack leading to crumbling of the pellet and total fracture can not be obtained[9] Often, the actual area of the granule where load is applied is difficult to estimate due to the spherical shape of the granules. Hence, determination of the crushing strength for aggregate purposes is rarely performed.

A test for evaluating the compression and crushing strength of the granules was improvised by utilizing the strength testing principles of ceramic powder materials. The design of the testing procedure is described in the section of agglomerates characterization in the first phase of the experiment.

Abrasion resistance is often used as a general index of the quality of the agglomerates.[6,26] Failure is evident through wearing of the exterior as a fine powder or breaking into small pieces. The most common test used is the the Los Angeles abrasion test (rattler method) performed in accordance with American Society of Testing and Materials (ASTM) C 131 or C 535. Briefly, a specified quantity of aggregates is placed in a steel drum with an abrasive charge of steel spheres, the drum is rotated subjecting the particles to impact and abrasion , and the percentage of material worn away is measured. Specifications has set a limit on the maximum allowable weight loss depending on the gradation and usage of the aggregates.

In most cases, the agglomerates are exposed to severe weather conditions, either in the landfill site or as aggregates. Therefore, freeze-thaw resistance is a very important characteristic of the green pellets. Failure is often characterized by expansion and disintegration into smaller pieces. The expansion caused by freezing and thawing has been expounded by many investigators and various theories have been hypothesized in trying to understand this phenomena.[27,28,29,30,31] Evidently, the particles absorb so much water, and eventually reach critical saturation point that the expansion and hydraulic pressure caused by freezing of water can no longer be accommodated. Approximately 9% volume expansion accompanies the freezing of water , expelling excess water from the cavities in the course of its movement. Once the dilating pressure exceeds the tensile strength of the aggregate, failure is imminent. In this regard, the pore structure, permeability, and absorption characteristics of the granules determine the degree of susceptibility factors to severe changes in weather. An excellent review of frost action and aggregate durability is available in literatures.

The resistance to disintegration by freezing and thawing can be evaluated through the method used by Iowa State Highway Commission (Materials Department) for testing aggregates (Test Method No. Iowa 211-A). Two procedures are followed depending on the quality of the aggregates. Method "A" is for higher quality aggregates and consists of thawing in a water-alcohol solution. Method "C" is intended for lower quality aggregates and uses water as the thawing medium. Of particular interest in this study is the latter method where the aggregates undergo 25 cycles of alternating freeze-thaw patterns. Disintegration is measured in terms of weight loss and should fall within the limits set by the specifications.

Porosity The term refers to the volume of the granule that is not occupied by solids,[32] ergo, pore space and such properties as size, shape and distribution within the structure. There are basically two types of pores namely the permeable voids and non-permeable voids. The difference is implied by the name itself, non-permeable indicates that no liquid can enter and occupy the void space.

The exact geometry, that is size and shape, of the pores is difficult to ascertain due to their irregular shapes and in their mode of production. In agglomeration of fly ash, the pores created by physical conditions are usually larger than those formed from chemical reactions. The reaction products formed during the hydration of fly ash act as solid hydrate bridges across the water-filled spaces. The distribution of the solid hydrates then constitute the relative proportion of the so called gel, a material of minimum porosity and high specific surface area.[33] The porosity resulting from the pore space not filled by the gel is termed capillary porosity. This volume thus decreases, and that of the gel pores increases, as hydration proceeds. Generally, capillary pores are larger (≥ 0.1 μm) than the gel pores and interconnected by smaller capillaries and gel pores. On the other hand, physical conditions like slope of the disc, particle size and shape, gradation of the feed influences the formation of large pores due to entrapped air or inadequate consolidation. These pores tend to limit the strength of the specimen but may not influence permeability of the sample.

The shape factor and size distribution affect the closeness and effectiveness of packing in the structure. A mixture of different sizes gives a lower voidage or porosity than a narrow size range. The small-sized particles tend to fit themselves in the voidage created by the larger ones. A marked reduction in porosity is thus observed if higher proportion of smaller spheres are introduced.

There is no standardized method for the measurement of total porosity. A common practice is determining the bulk specific gravity, G_b, and the true specific gravity, G_t of the aggregates. The former is defined as the ratio of the oven-dry weight in air of the solid sample at 73.4°F to the weight of water displaced by the particle in its saturated surface-dry state.[32] The oven-dry weight divided by the volume of solids excluding all pores provides the true specific gravity of the sample. A general rule for porous material is that the greater the porosity of the aggregate, the greater are the differences between the various specific gravities. Figure 2 shows the different states of moisture in an aggregate which are required in the calculations of relative densities. Test method for determination is described in ASTM C127 on an oven-dry or saturated surface dry bases.

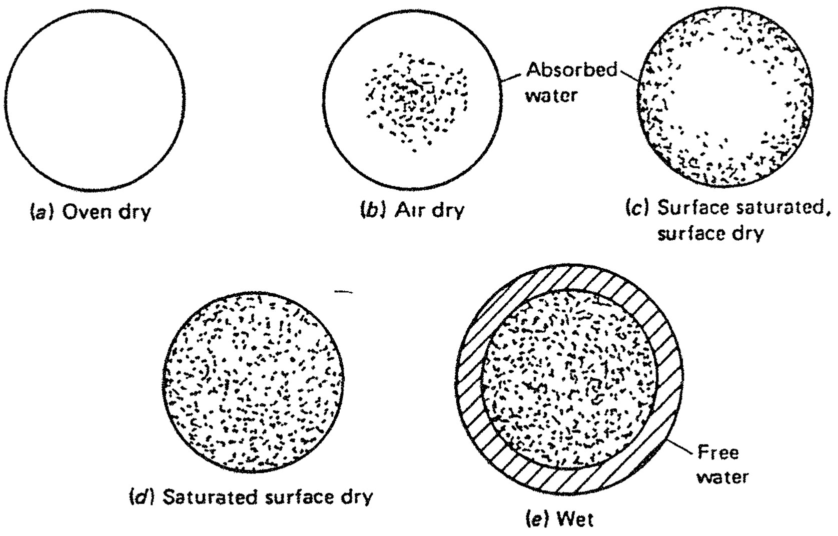


Figure 2. States of moisture in an aggregate. Total moisture: (a) none; (b) less than the absorption capacity, drying; (c) less than the absorption capacity, absorbing; (d) Absorption capacity; (e) Greater than absorption capacity.

The porosity (p) is then calculated as follows: [32]

$$p = 1 - (G_b / G_t) \qquad \text{Eq'n. 1}$$

The problem with this lies on the accurate determination of the true specific gravity. It is difficult to measure the true volume of the voids due to the presence of the non-permeable pore spaces.

In investigating permeable voids or effective porosity, the absorption capacity of the sample is measured.[26,32,33] The volume of water absorbed is assumed equal to the pore volume and complete saturation has been reached. The usual procedure is in accordance with ASTM C 127-88 where the aggregates are immersed in a pan of water for 24 hours.

An alternative to the pore structure measurement is the visual testing of a polished and thin section of the granule by photomicrographics method or electron microscope. The scanning electron microscope allows the calculation of the surface area of the particles through its feature analysis program.[34,35,36] Morphological as well as chemical information from the sample can be extracted during and after the acquisition of digital images. However, sample preparation involves time and effort due to the shape of the granule itself. The cost of running the test is a major limitation.

An indirect technique for the determination of the porous properties of solids utilizes mercury porosimetry.[37,38,39,40] In this apparatus, mercury is forced into the evacuated sample with the application of increasing pressure. Volume changes are monitored by measuring the mercury level in the stem of the sample tube. The principle of Laplace equation is applied in measuring the pore neck size and body through intrusion and extrusion data. The surface area of all pores and voids filled by mercury is obtained from the intrusion data as a function of the applied pressure. The extrusion data provides the pore size distribution curves against pressure being released. With the exception of surface area, the pores are assumed to be cylindrical in shape.

Mercury porosimetry is so far the only recognized ASTM standard for determining pore distribution. Standard equipment is therefore available commercially. Another advantage is that it takes only about half an hour to complete the test. However, mercury porosimetry has the following restrictions: [42]

1. The small sample size required is not representative of the material.
2. The body size distribution of the pores can not be evaluated due to the entrapment of mercury inside the body during the extrusion process.
3. Isolated pores may not have been measured and so the neck size distribution may be false.
4. The contact angle of mercury actually depends on the nature of the porous matrix. Therefore, it should be determined for each solid sample.

5. The application of high pressure could alter pore geometry and therefore could give false reading.

Even with these disadvantages, it is still the popular choice for evaluation of the pore structure of the granules. Interpretation of the data necessitates careful consideration and analysis.

Leachability The potential for releasing trace metals and other potential health hazards to the environment is the most important criterion in the stabilization of waste material. Technical definition of leaching is the process by which a component of the waste is removed mechanically or chemically into solution from the solidified matrix by the passage of a solvent such as water.[43,44] Several factors affect the leaching characteristics of an agglomerated waste, namely pH, stoichiometry, temperature, ions present, oxidation-reduction potential, and many other complex reactions occuring in the system.[43,44,45,46] Physical properties such as durability and permeability can catalyze or retard the leaching process. Clearly, the long term physical integrity of the agglomerates is an important consideration for a waste treatment process.

The maximum hazard posed by a stabilization process can be assessed using different regulatory testing methods. The most accepted is that of the Toxicity Characteristic Leaching Procedure (TCLP), designed to determine the mobility of both organic and inorganic pollutants present in the solid or liquid waste.[44] The Environmental Protection Agency (EPA) requires that samples be tested as smaller pieces passing through a No. 100 mesh standard sieve and subsequently mixed with an extracting fluid (either acid or water). The resulting extractants are then analyzed for potential contaminants. The concentrations of these contaminants should pass the national drinking water standards where two classifications exist, the first being a suggested limit and the latter a maximum allowable limit. The maximum concentration of contaminants allowable in the TCLP test is 100 times the National Primary Drinking Water Standards. Leachates containing greater than this level cause the waste to be considered hazardous and be subject to regulatory provisions. Leachates with lower level are classified as non-hazardous.

Stabilization and Solidification

In this section, it is important to define and, at least, differentiate stabilization from solidification. The fundamentals of these treatment methods have to be established in understanding the whole scheme of the encapsulation technique developed in this study. Immobilization of the heavy metal compounds consisted of using the hardening properties of fly ash and proceeded by agglomeration.

Stabilization techniques primarily refer to treatment methods that limit the solubility or mobility of the contaminants with or without the improvement in the physical properties of the waste.[44,45,48,49] It usually incorporates materials that ensure that the hazardous components are maintained in their least mobile or toxic form. This form of treatment is usually accompanied by a change in the chemical state of the toxic constituents.

Solidification, on the other hand, generally implies the formation of a solid mass of waste with high structural integrity.[45,49] The pollutants are mechanically interlocked within the solid matrix and do not have to chemically react with the other compounds to immobilize them. Leaching is reduced, if not prevented, by the reduction in the surface area exposed to the environment.

Another commonly used term is fixation, which refers to any of the stabilization and solidification processes. The overall objectives include improving handling characteristics, reducing leaching potential, and limiting the solubility of the toxic components in the waste.[47] In this particular case, the high calcium fly ash cementation process is applied to a metal rich sludge waste, incorporating the waste as part of the rigid matrix. Lime, in combination with fly ash provides cementitious matrices in physically and chemically entrapping the waste. Inclusion of lime in the matrix not only provides gain in strength but also renders the pollutants less soluble in a highly alkaline environment.

Regulatory basis of the fixation method

Stabilization of waste is specifically included in the National Oil and Hazardous Substances Contingency Plan (NCP) (Federal Register, 40 CFR 300, 1982) as a treatment method for hazardous wastes. It states that all alternatives to remedial action should be evaluated. Costs and engineering considerations are critical to these evaluations. Environmental and public health factors are also prime considerations in the selection of a feasible treatment method.

The chemical reactivity of the waste generally controls the selection of waste stabilization and solidification options. Major chemical considerations in the selection process have been extensively monitored and indicates the suitability of cement- and pozzolanic based-materials in the treatment of waste.[5,43,45,47,48,49,50]

Stabilization/solidification of waste using pozzolanic material requires careful selection of the reactive fly ash. Standard testing systems (ANSI/ASTM C 311-77) and standard specifications exist for fly ash (ASTM 1973) which takes into account both chemical and physical properties.[49] These criteria have been established to specify the properties that a particular ash must exhibit in order to perform adequately in the given application. By using fly ash that meets the specifications, pozzolanic activity greater than the specified minimum is guranteed.

Specifications for stabilized/solidified wastes

There are no standard testing procedures developed for the treated waste. However, they should be evaluated in terms of their leachate potential, physical stability under burial conditions, strength or bearing capacity, permeability of the waste, and weathering resistance.

These have all been discussed in the previous section including the corresponding tests for each property. These performance testings of trial mixes must be completed to evaluate the suitability of fly ash in the final product.

EXPERIMENTAL APPROACH

This study is divided into two phases. The initial phase dealt with establishing the optimum conditions for the agglomeration of fly ash as a means of stabilizing hazardous wastes. The variables considered were moisture content, speed of revolution, feed rate, and residence time. It also identified fly ash and cement kiln dust as suitable stabilizing agents from among the waste products available, and determined possible proportions for blending that would give the desired end product characteristics. The effect of granule size in establishing the optimal conditions of high strength granules was also investigated. Due to environmental implications of using toxic waste in the investigation and ending up with a large mass of agglomerated waste, a simulated sludge was used to control the variables for agglomeration. In this stage, the schematic flow of the whole experiment was established.

The second phase involved the use of electroplating sludge in the agglomeration process of fly ash and fly ash-kiln dust mixtures at the optimal operating conditions using two different types of Class C fly ashes. The effect of different curing conditions and different proportions of fly ash and kiln dust in the inner kernel and outer layers of the granules in relation to the physical integrity and durability of the agglomerates were carefully assessed. In addition, the electroplating sludge was agglomerated with and without the pre-conditioning step practised in the first phase. The importance of pre-conditioning was therefore established, coupled with the right blend of fly ash and kiln dust that may be used for future work. Testing procedures were developed based on the standard methods in response to the limited quantity of agglomerates available. Finally, correlations between the two testing methods were performed with the use of Department of Transportation (DOT) tested aggregate.

Materials and Characterization

Regulatory classification

Non-hazardous wastes are regulated under Subtitle D of the Resource Conservation Recovery Act of 1976 (RCRA), which allows individual states to provide their own regulations regarding disposal practices. Fly ash is considered non-hazardous by RCRA and guidelines are provided regarding the use of fly ash in cement and construction industries under Section 6002(e) of RCRA.[33] This section requires procuring agencies using appropriated federal funds to purchase items composed of the highest percentage of recovered materals practicable. Incorporation of fly ash in construction purposes is highly encouraged to be executed at the maximum extent.

On the other hand, RCRA strictly controls and monitors the generation, treatment, and disposal of hazardous wastes under Subtitle C. It lists specific wastes as hazardous and should therefore be stored, transported, and disposed in accordance with the federal regulations. Electroplating sludge, which was used in this study, is specifically listed as hazardous under Subpart D in 40 Code of Federal Regulations (CFR) 261. 31. Its designated EPA hazardous waste number is F006.[50] The presence of cadmium, hexavalent chromium, and nickel are the toxic components for which it was listed, although higher concentration of zinc, copper, and other heavy metals than those specified in the regulations also cause it to be classified as such.

Fly ash

High calcium fly ashes were obtained from the Ottumwa and Lansing power plants. The coal source is a low sulfur subbituminous coal from the Powder River Basin near Gillete, Wyoming. The physical and chemical properties of these fly ashes have been closely monitored in previous experiments and indicate slight differences in their chemical compositions.[51] The bulk mineralogy of the fly ashes were also determined by X-ray diffraction (XRD) technique and identified similar major crystalline compounds. Since particle size distribution of the fly ash is an important parameter in agglomeration, Figure 3 shows a typical gradation curve of the two fly ashes. The Laser particle size analyzer was used measuring particle size finer than No. 100 mesh sieve.

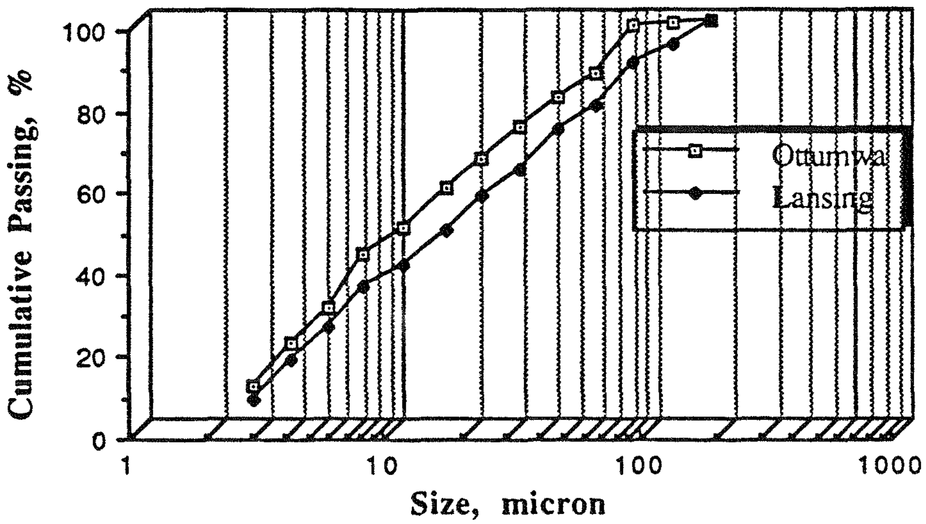


Figure 3. Gradation curves of Lansing and Ottumwa fly ashes

Results of the chemical and physical analyses of both fly ashes are shown in Table 1. Both fly ashes exhibit almost the same physical properties based on ASTM C 311 standard tests. Slight variation in analytical lime content is apparent from the data. Chemical compositions fall within the specified range of a Class C fly ash, having $SiO_2+Al_2O_3+Fe_2O_3$ over 50% for both fly ashes. Available alkalies are expressed as Na_2O equivalent.

However, significant differences are observed in the properties of the paste made from water-fly ash ratio of 0.27. There is a wide range in the compressive strengths, with an average of 5190 psi for Lansing samples and 1400 psi for the Ottumwa samples. Initial and final setting times were also noted to vary in a wide range. These results are mainly due to the

Table 1. Chemical and physical properties of fly ashes[52]

	Lansing	Ottumwa
Chemical Oxides		
CaO	30.0	25.4
SiO_2	30.7	33.8
Al_2O_3	16.5	20.0
Fe_2O_3	6.70	5.40
Na_2O	1.76	2.01
K_2O	0.26	0.36
MgO	6.3	4.60
SO_3	3.6	2.4
Physical (ASTM C 311)		
Moisture (%)	0.2	0.0
LOI (%)	0.5	0.3
Fineness (%)	13.1	12.1
Specific Gravity	2.76	2.62
7 day pozz with cement (%)	92	96.0
28 day pozz with cement (%)	92	97.0
Pastes @ W/FA = 0.27		
Compressive Strength (psi)		
1 day	3580	520
7 day	5730	720
28 day	5740	740
Autoclave Expansion (ASTM C490)		
Expansion @ 28 days (%)		
Air cured	-0.095	-0.016
Humid cured	0.051	0.00
Setting Time (Vicat), (mins.)		
Initial	8	20
Final	10	30

difference in the relative amounts of reactive glass phases present in the two fly ashes, despite their very similar chemical compositions.[3,52]

Figure 4 illustrates typical x-ray diffraction (XRD) patterns of the fly ashes. It confirms the presence of quartz, periclase, anhydrite, and tricalcium aluminate as the major crystalline phases. The difference between the two patterns is in the relative intensity of the peaks which may imply the preponderance of the crystalline material in Lansing fly ash. As noted earlier, both fly ashes contain an appreciable quantity of lime. Of particular interest is the highly skewed background pattern at about 30° 2θ (Cu radiation) for the Lansing and around 28° 2θ for the Ottumwa, fly ashes. This behavior is highly characteristic of the amorphous nature of Class C fly ashes and can be attributed to the presence of a calcium aluminate or a calcium aluminum silicate glass.[53] Studies also indicate that the angular position of the glass x-ray diffraction maximum increases linearly with CaO content, suggesting a progressive modification of the siliceous glass structure with increasing calcium content.[33,53]

Illustrations of the basic spherical shapes characteristic of most fly ash particles are shown in Figure 5. Some particles can be observed to contain powdery deposits on their surfaces while some remain to be virtually free of these surface deposits. .

Kiln dust

Kiln dust was obtained from Lehigh Portland Cement Company in Mason City, Iowa. The chemical analysis is given in Table 2, which manifests a high alkali content, particularly potassium oxide (K_2O). Analytical calcium is approximately 52% based on x-ray fluorescence analysis while temperature rise reading, ΔT, of 9.9 °C corresponds to 20% lime in the sample. Trace metals analyses warrant a relatively low concentration of chrome, nickel, and zinc to exacerbate potential leaching problem in the treatment of the metal-rich sludge. It consistsprimarily of fine particles with 92% passing No. 100 mesh sieve to effect proper agglomeration with fly ash.

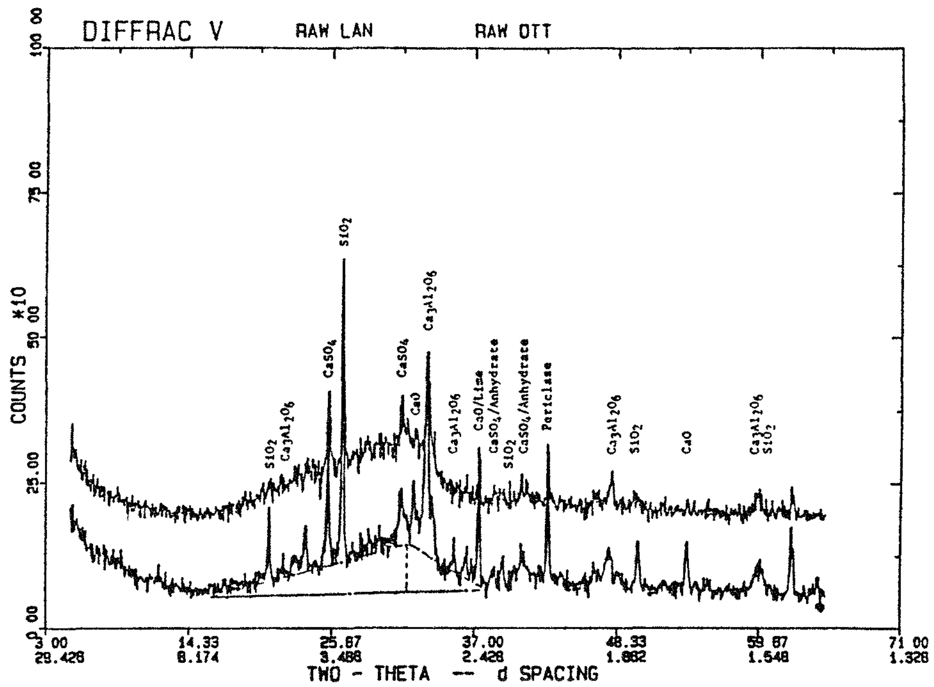


Figure 4. Typical x-ray diffractograms of Lansing and Ottumwa fly ashes

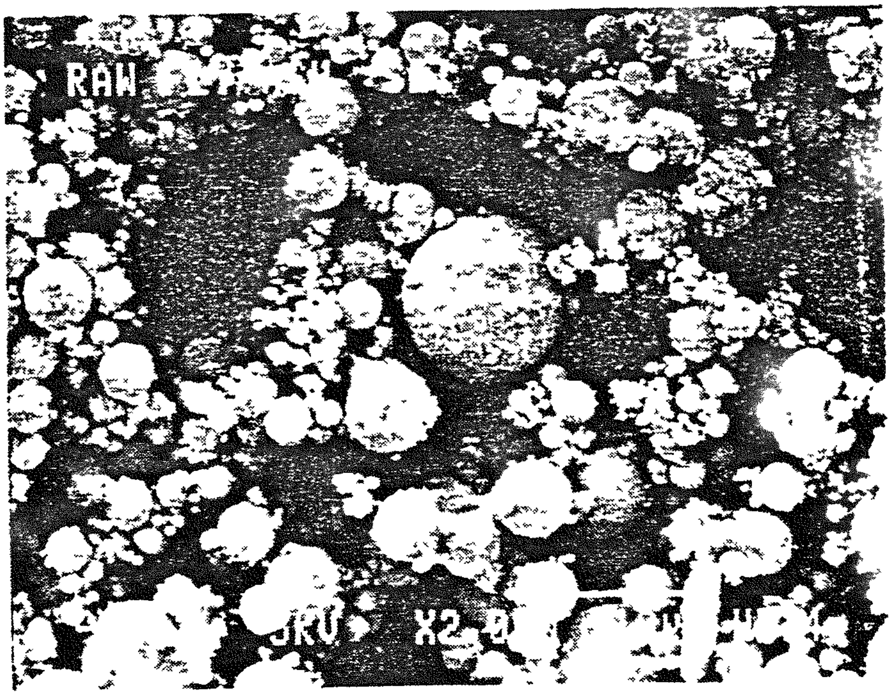


Figure 5. Morphology of high calcium fly ash

Table 2. Kiln dust analysis[55]

Major/Minor Elements		**Trace Elements**	
As Oxides	Wt., %	Element	μg/g (ppm)
CaO	52.2	Cd	< 5
MgO	2.0	Cr	42
Al_2O_3	4.4	Mn	160
Fe_2O_3	1.9	Ni	40
SiO_2	14.2	Pb	930
TiO_2	0.2	Zn	190
Na_2O	0.2	Temperature Rise , ΔT= 9.9 ^{o}C	
K_2O	9.0	Ignition loss @ 950^{o} C = 2.2%	
SO_3	12.2	Specific Gravity = 2.897	
<u>Sieve Analysis (% Passing)</u>			
#100 = 91.8			
# 200 = 70.0			
# 325 = 35.4			

X-ray diffraction pattern shown in Figure 6 illustrates the preponderance of lime in the sample. Minor crystalline substances also exist in the form of quartz, calcite, arcanite, and some forms of edenite and a calcium magnesium aluminum silicate. Identification of the other calcium-bearing compounds substantiates the high calcium concentration as measured by x-ray fluorescence.

Simulated sludge

The simulated sludge was prepared to contain the principal heavy metals present in the electroplating sludge under investigation. It was made from soil, tap water, and solutions of varying amounts of nickel nitrate, copper nitrate, and zinc chloride, which are the heavy metals of interest in this study. Initially, these heavy metal salts were dissolved in deionized water before adding them into the soil. Approximately 1000 grams of soil was used per batch and the final moisture content was brought to 60% by weight of soil. Determination of the initial water content of the soil was therefore a prerequisite to the preparation of the simulated sludge. The amount of water was made on the premise that typical solids content of the electroplating sludge after dewatering is around 20-50%.[52,53] Others report sludge cake solids content in the range of 50-70 percent by weight.[52] The cake solids content varies depending on the dewatering device being used. Initial trials of using the lower range of the solids content only resulted in using more fly ash for solidification. Solids content of 40% seemed adequate to provide the initial chemical reactions between the heavy metal salts and fly ash components prior to agglomeration. In this way, the metal salts were converted into some forms of their metal hydroxides. To ensure uniform mixing and prevent coagulation, a Hobart Model C-100 mechanical device was adopted.

The approximate concentrations of zinc, copper, and nickel present in the simulated sludge are reported in Table 3. The soil itself had average concentrations of 82.74 ppm, 21.1 ppm, and 13.64 ppm of zinc, nickel, and copper respectively. Concentrations remained nearly

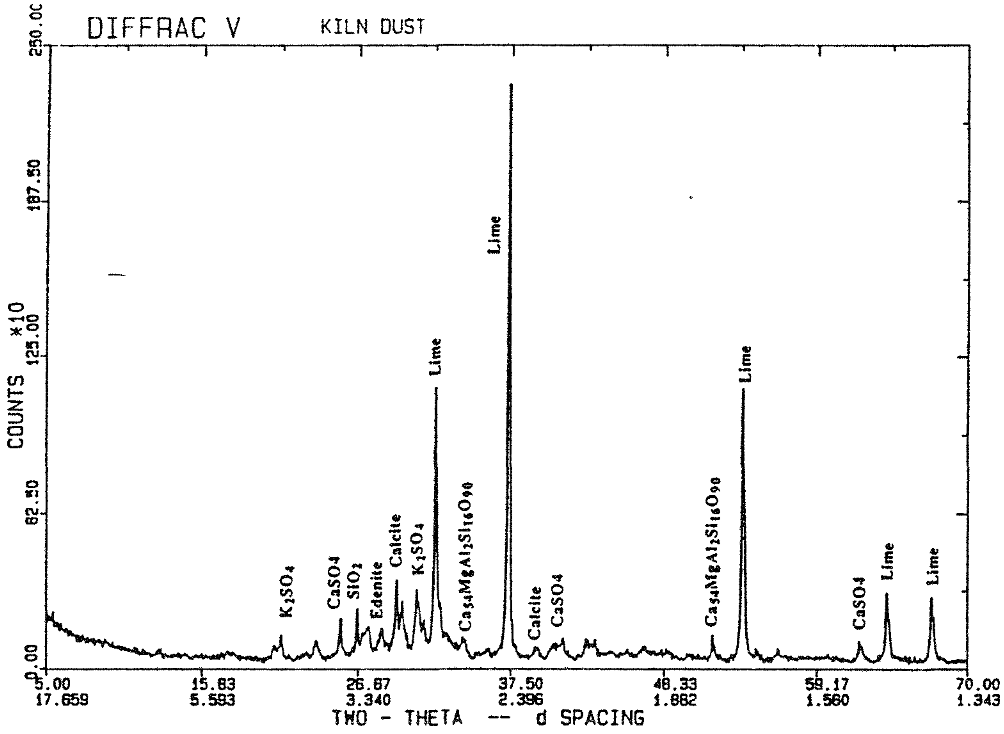


Figure 6. X-ray diffractogram of Lehigh cement kiln dust

Table 3. Concentration of zinc, copper, and nickel present in the simulated sludge

Trial No.	Zinc (ppm)	Copper (ppm)	Nickel (ppm)
1	783	1259	321
2&3	706	324	271
4	8, 083	2, 714	3, 375
5	27, 359	11, 487	14, 951
6&7	651	240	302
8&9	661	244	307

constant for trials 1-3 and 6-9, with the exception of copper in the first trial. Pure copper was substituted for copper nitrate since the latter was not available at that time. Lower concentrations of these metals relative to the amount in the real sludge were deliberately done due to the sensitive nature of the waste. For leachate analysis, trials 4 and 5 were prepared using higher concentrations of each of the three metals. This would negate assumptions that initial concentrations were already below the limits of standard leaching specifications. The same samples were subjected to XRD and scanning electron microscope for identification of possible stabilization reactions with fly ash and kiln dust.

The x-ray diffraction pattern of the simulated sludge used in most trials is shown in Figure 7. The major phases identified were quartz and some clay minerals such as muscovite and anorthite. Metals concentration for trials 1-3 and 6-9 were below 1000 ppm to be detected by x-ray diffraction.

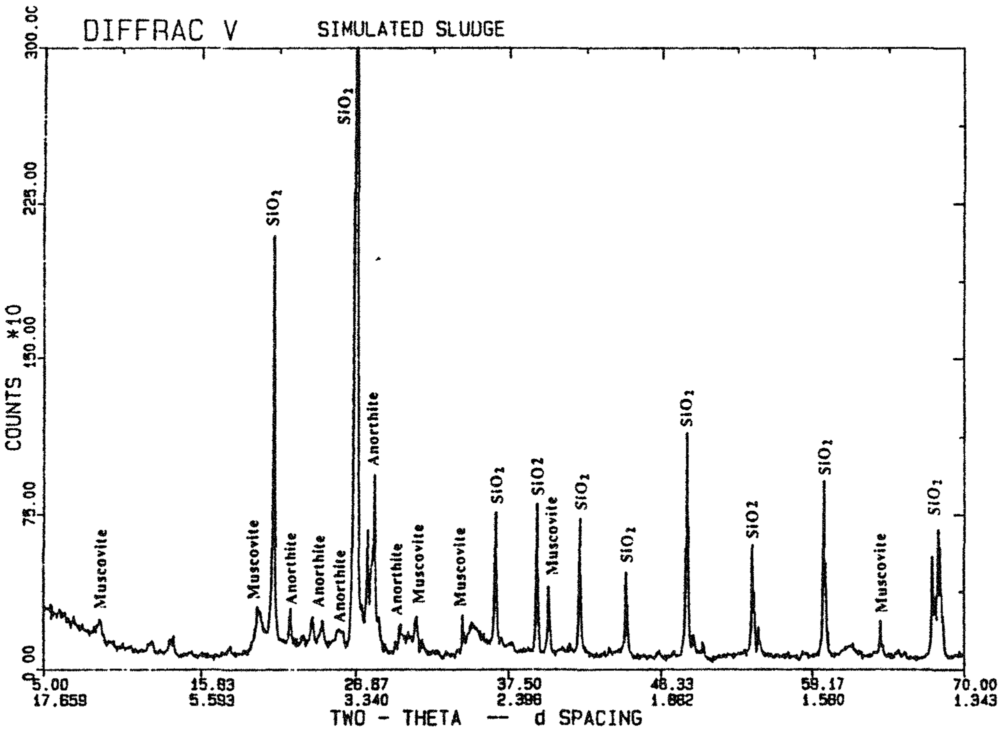


Figure 8. X-ray diffractogram of simulated sludge

Electroplating sludge

The electroplating sludge was taken from a company in Minnesota using copper, nickel, chromium, and zinc on plating ferrous, nonferrous, and plastic materials. A chemical analysis of their sludge sampled on July 15, 1990 is given on Table 4. Quantitative chemical analysis by X-ray fluorescence (XRF) technique was carried out by using special standards prepared in the laboratory. It should be noted that the concentrations can vary per plating batch depending on the materials being plated and the thickness of the coating.

The x-ray diffraction pattern for the electroplating sludge is shown in Figure 8a. It shows calcite as the major crystalline component which is expected since lime was used in precipitation of the metal hydroxides from wastewater. Different forms of iron hydroxides can be discerned from the pattern which explains the diffraction "halo" characteristic of amorphous materials. Chromium hydroxide hydrate is also observed which is not improbable owing to the high concentration of chrome in the sludge. There are "chunks" of black solid material in the sludge which are observed to be inside some of the granules. An analysis of such chunks showed them to be made up of goethite ($FeO(OH)$) and sodium calcium aluminate oxide.

In order to ascertain the presence of hydroxide compounds in the sludge, the sample was ignited to a temperature of 1200°C. The fired sample was subjected to XRD analysis. Figure 8b shows the oxide compositions of the electroplating sludge after thermal decomposition. Iron oxide, chromite, lime, periclase, and zinc oxide are among the compounds detected. Some forms of calcium chrome silicate and calcium zinc silicate are most likely present. Formation of these compounds may be ascribed to the high adsorption capacity of calcium silicates for amphoteric metals such as zinc and copper. Calcium silicates may have been generated during the decarbonation of calcite into lime and carbon dioxide at high temperature, with lime subsequently reacting with the available silica from the sample.

Table 4: Chemical assay of electroplating sludge (2/16/90)

Elements	Concentration (%)
Potassium	0.04
Aluminum	0.24
Arsenic	< 0.003
Barium	0.05
Cadmium	<0.003
Chromium	16.27
Copper	0.77
Iron	19.18
Manganese	0.15
Nickel	4.24
Lead	0.37
Selenium	< 0.003
Tin	0.12
Zinc	11.77
Sodium	1.11
Calcium	8.30
Magnesium	1.38
Cyanide	10.0 mg/kg
Titanium	0.02
Strontium	0.03
Silicon	3.08
Phosphorus	1.88
Sulfur	0.79
Moisture Content	39.855

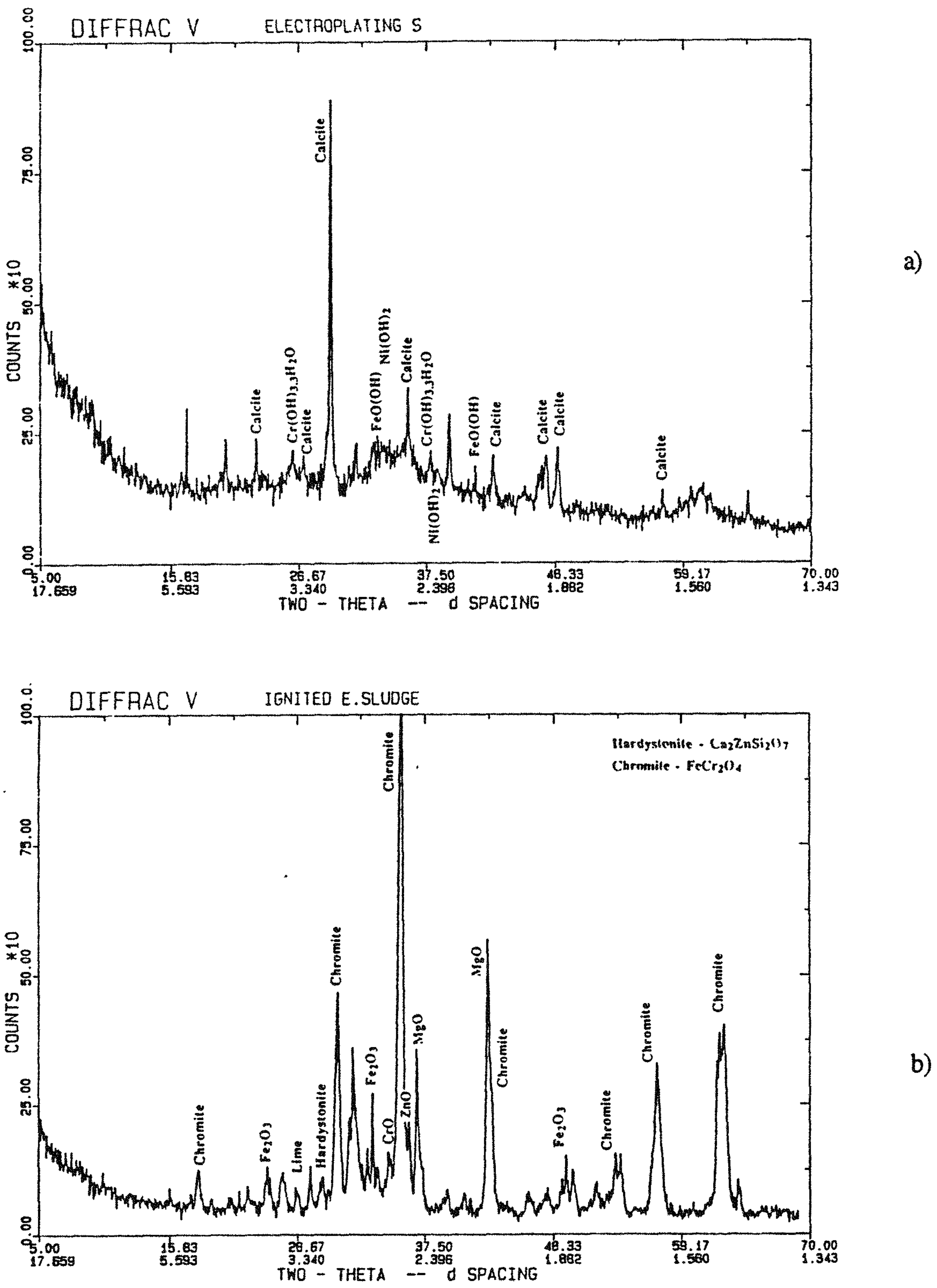


Figure 8. X-ray diffractogram of electroplating sludge a) unfired sample, b) ignited samples

Amphoteric adsorption of heavy metals onto silica surfaces has been well documented and the conditions described warrant such reactions to occur.[56]

Pan Agglomeration

In this study, a rotary pan agglomerator manufactured by Mars Mineral Corporation, model no. DP-14 "Agglomiser", was used in the production of the green granules. Its depth measures 15.5 cm with an inside pan diameter of 36 cm. It was made from type 304 stainless steel of 14 gauge thickness and designed to provide variable speed and angle of the disc pan. It is a bench scale unit ideal for batch method of operation and small scale evaluation of the agglomeration process.

The disc is driven by an adjustable DC motor of type Baldor, with 1/8 HP, 60 cycle, 120 voltage rotor. The pan speed can vary from 0 to 50 rpm. Pan angle can vary from 35 to 90^{o} from the horizontal using a machinist's protractor.[23]

The materials are discharged to the pan using a vibratory feeder with a 2-liter capacity surge hopper, Model FTOC, and crafted by Syntron FMC Corporation. In order to control the rate of solid flow, a constant quantity of feed was maintained for all trials. The time for all the solids to be discharged double checked for any change in the feed rate during the run.

In the absence of automated water spray and scraper system, these variables were controlled manually. Moisture was added using a spray bottle which had been initially calibrated. The actual amount of water and the position of water addition which would effect proper agglomeration were carefully monitored throughout the run . For scraping purposes, a steel trowel and spoon were employed to prevent solid build-up on the sides of the wall.

PHASE I: OPTIMIZATION OF AGGLOMERATE FORMATION

Experimental Procedure

Trial batches of simulated sludge were prepared as described in the materials section. A trial batch consisted of five different tests ran under the same conditions except for that variable being optimized. The first four trials used pure fly ash in solidifying the simulated sludge while trials 5-8 made used of kiln dust. In both cases, the optimum moisture content, angular velocity of the disc, and retention time, as a function of granule strength were determined. The effect of feed rate was also investigated using the fly ash-simulated sludge mix. A pan angle of 50^o from the horizontal was adopted based on earlier experiments by Burnet.[13,15] The particle sizes in the sludge/fly ash mixtures were constant throughout the trials.

The initial step was to solidify the simulated sludge while maintaining thorough mixing. The amount of kiln dust required for solidification was considerably lower due to its higher lime content compared to fly ash. Approximately equal amounts of fly ash was used in this step as opposed to about 800 grams of kiln dust. The use of these materials caused absorption of excess moisture and initiated hydration reactions among metal salts, fly ash, or kiln dust compounds. The particulated simulated sludge was allowed to set prior to agglomeration. This was subsequently ground and broken into small pieces. Moisture content at the end of solidification stage was around 26%.

Approximately 500 grams of the solidified sludge were directly charged into the pan while an equal amount of fly ash was placed into the feed hopper. The particulated sludge acted as nuclei for agglomeration and the fly ash provided further layering and growth of the granules. For the first trial, moisture content was varied from 7-23% while keeping default settings at 35 revolution per minute (rpm), 30 grams per minute feed rate, and 2 minutes retention time. For the second trial, retention time ranged from 1-5 minutes, in one minute intervals. However, it should be noted that retention time refers to the additional compaction time for the granules to remain in the disc even after all the feed had been discharged. This particular test evaluated the effect of longer agglomeration time on granule size and strength. A moisture content of 14-16% was maintained in all trial runs. Lastly, the third trial varied the angular speed from 30-55 rpm with all other parameters constant. Each run lasted for about 30 minutes or longer depending on the agglomerating conditions. The granules were then removed manually from the pan and separated according to sizes using the U.S. standard sieves. Three sieve sizes were adopted such as 1/2", 3/8", and #4 mesh sieves. Those granules greater than 1/2" and passing #4 were discarded and control sizes were limited to 1/2", 3/8", and #4 sieve size (0.187 ").

A second agglomeration was also carried out in case improper coating had occured or less durable granules formed. However, about half of the granules formed in the first agglomeration were allowed to air-cure for strength testings. The other half was prepared for the second agglomeration. This step proceeded according to sizes for each trial run, using equal proportions of fly ash and singly-agglomerated granules. Re-agglomeration according to granule sizes enabled a more uniform coating and at the same time prevented crushing of smaller granules by the larger ones. The amount of moisture added was maintained at 14-16%. In effect, the proportion of simulated sludge to fly ash at the end of the first agglomeration was 1:2. Re-agglomeration formed granules of 1:3 sludge to fly ash ratio.

The purpose of the fourth and fifth batches were primarily to investigate the effectiveness of using fly ash as a stabilizing agent. A higher concentration of heavy metals were present in the sludge and it was subsequently solidified with either fly ash or kiln dust. The fourth trial used fly ash for solidification and agglomeration while the fifth one used kiln dust for solidifying the sludge and fly ash for agglomeration/layering. As always, equal amounts of the solidified sludge and the fly ash were used in the re-agglomeration process and the default settings were unchanged.

Trials 6-8 proceeded in the same manner as trials 1-3. The main difference was using kiln dust in preconditioning the simulated sludge. Fly ash was still the agglomerating material and, in effect, the proportion of kiln dust used was approximately 22% by weight at the end of the first agglomeration. Moisture content was kept constant within the range of 12-14% for trials 7 and 8. Initial findings of using pure kiln dust in the solidification stage proved futile and produced cracking in the granules. Double agglomeration was tried at this point, still using fly ash. Percentage of kiln dust was then maintained at approximately 11% by total weight of the mixture.

The effect of reducing the proportion of kiln dust to 30% in the solidification stage was then investigated in trial 9. Moisture content was varied and fly ash was used for agglomeration.

Since the agglomeration process involved in this phase consisted of three stages of moisture addition, it was necessary to simplify calculations of percent moisture in the agglomerates. Moisture content of the solidified simulated sludge was essentially fixed for all trials. Variation was only introduced during the actual agglomeration. Therefore, for the first agglomeration, moisture content was estimated based on the amount of fly ash used for granulation of the solidified simulated sludge. Percent moisture for the second agglomeration was calculated based on the overall quantity of fly ash used in both agglomeration steps.

The final batch trials consisted of finding the feed charge rate which would give maximum granule strength. Agglomeration was carried out with the feed charge rate ranging from 20 - 50 grams per minute while keeping all other variables constant. Trials proceeded without the double agglomeration step and using only fly ash as the solidifying and agglomerating agent.

Characterization of Agglomerates

In order to evaluate the physical and chemical durability of the green pellets, the following parameters were determined: a) relative estimate of the crushing strength of the granules, b) leaching potential of the agglomerates using EPA standard TCLP test, c) crystalline phases present in the agglomerates by x-ray diffraction, using a Siemens D500 diffractometer, and d) morphological characterization of the granules using a Jeol JSM-804A Scanning Electron Microscope (SEM). The crushing strength testing procedures will only be discussed.

Crushing strength

The physical stability of the granules under conditions of burial is necessary to ensure that they can support the required load either in a landfill site or as road/base aggregates. The crushing strength of the agglomerates were measured using the Tinius Olsen Universal Testing Machine with a maximum load capacity of 90, 000 lbs. The tests were run for each granule at a constant rate of approximately 20 psi per second and the load of failure was digitally recorded. The control size for testing was 1/2" and an average of 8 to 10 samples were used per trial. The physical dimensions of the granules and the orientation on which the load was applied were carefully taken into account and were recognized as limitations of the testing procedure. In so doing, the results of the tests only give a rough estimate on the trend of the strength development based on different agglomeration variables.

In order to minimize the effect of particle size and shape of the granules, a crushing strength test was improvised based on the principles of ceramic powder compaction. Compaction of ceramic powders involves the rearrangement of essentially nondeformable particles which usually are in the form of agglomerates.[57] It only seems natural for the harder granules to be crushed or deformed at higher applied load. In essence, the compaction behavior of the ceramic powders is strongly dependent on the nature of the agglomerates and the binder.[57] It is sensitive to the size and shape of the agglomerates or rather in the state of agglomeration of the powder.[58] In this regard, compaction pressures are used to characterize the strength of the agglomerates. Compressing harder agglomerates result in a decrease in the compact density, which is due to the collapse of the large interagglomerate voids as they get crushed.[58] Increase in compact density can only be principally achieved from the elimination of the large void spaces during rearrangement.

Compaction curves are used to interpret the consolidation of ceramic powders where the green bulk density is plotted as a function of the logarithm of the applied pressure.[59] The semilogarithmic relationship observed for granulated powders is analogous to the semilogarithmic relation between the mechanical strength (s) of the brittle materials and their density as follows:[60,61]

$$s = s_0 e^{-bp}$$

where s_0 is the strength of the non-porous body, b an empirical constant and p the pore fraction. This equation indicates that the pressed density is directly proportional to the logarithm of the pressing pressure. Therefore, a plot of pressed density against the logarithm of the applied pressure gives a linear relationship. A breakpoint in the linear portions of the curve denotes the "yield pressure" corresponding to the onset of plastic deformation of the granules, and crushing commences.[59] This point is then taken as the measure of the strength of the granules. Figure 9 illustrates a pressure-density curve showing the breakpoint pressure of a granulated powder. The joining pressure is interpreted as the point at which the coarse intergranular pores are eliminated.

The compaction curve generates two linear slopes where the breakpoint gives the division of two regions. The first region is the linear portion of the curve at lower pressure

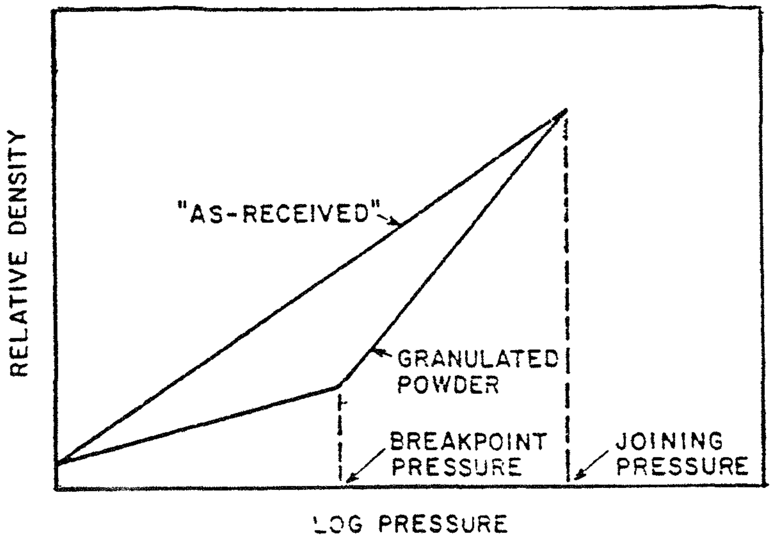


Figure 9. Typical pressure-density compaction curve of granulated powders[62]

where compaction is believed to be due primarily to particle rearrangement controlled by particle-particle friction.[61] The packing of the particles and the cohesive strength of the granules also control the compaction behavior at this stage. The second region begins after the breakpoint in the curve. The change in the slope is interpreted as an index of the fracture stress of the aggregates leading to continued sliding and rearrangement.[64]

The fundamentals of the pressure-density compaction curve were applied in the qualitative analysis of the agglomerates. In the present work, the determination of agglomerate strength by measuring the changes in slope during compaction was explored. Initial testings on the agglomerates gave reproducible results. The testing procedures were established after a series of trials, using available facilities in the laboratory. However, it should be emphasized that this method only indicates qualitative measurement of the relative strength of the granules.

The weight of the samples were initially taken before placing in a sample mold. The sample mold consisted of a steel ring with an inside diameter of 2.81" and a height of 3.5", mounted on a piston with the use of temporary spacers. The piston has a 2.78" diameter and is about 2.5" high. The sample mold was lubricated prior to testing in order to reduce pressure gradients and effectively increase the pressure near the bottom of the compact. Compaction density variations were then greatly minimized. The granules were placed in the steel ring mold in layers, carefully rodding each layer several times. Sample height should not exceed the diameter of the mold. This is particularly important in maintaining a uniform loading on the samples and also in preventing the concentration of the load in the center. A cross-sectional design of the sample holder is shown in Figure 10.

The weight of the granules in the ring mold was taken prior to testing, including the initial volume occupied by the granules. Afterwhich, the pressing operation was completed using the Tinius Olsen Universal Testing Machine. Load was applied at a constant strain rate of 0.05"/min and the transmitted load was digitally recorded. A dial indicator was used to measure the corresponding strain. The temporary support were immediately removed after several load applications, converting the sample holders into double acting pistons.

With the geometry of the steel mold and the initial height of the samples known, it was possible to back-calculate for the relative compacted density of the agglomerates at a given load. A typical pressure-density curve generated from the data is shown in Figure 11.

The compaction behavior of the agglomerates can be summarized into three stages. The first stage is a rearrangement of granules which shall be termed as seating deformation. This may be due to breakage of weak particles or irregular pressure distribution due to random voids. The point of inflection in the curve is the onset of failure or deformation of the agglomerates. The slope of this curve characterizes the behavior of the sample at compression and shall be referred to as compression stage. Finally, another break can be observed which indicates the breakpoint pressure of the agglomerates. This zone shall be termed as the crushing area or region of disintegration. If the test had been allowed to go further, another zone will be defined which is analogous to the joining pressure of typical ceramic powders

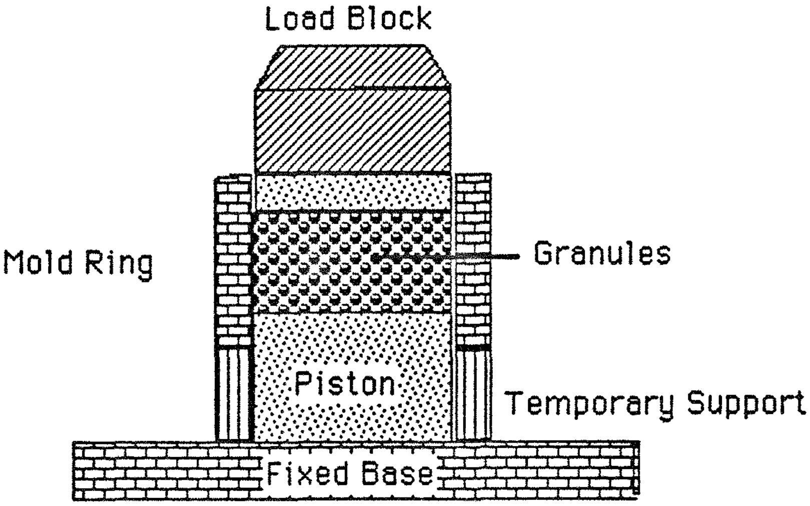


Figure 10. Cross-sectional view of the crushing strength set-up.

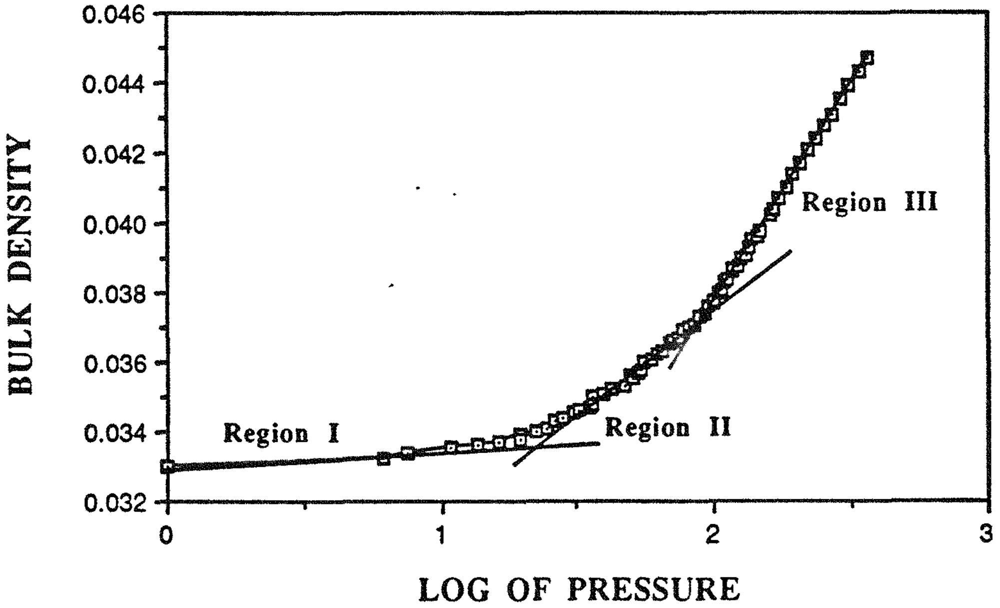


Figure 11. Pessure-density compaction curve generated from laboratory tests

compaction curves. This indicates the removal of large voids in the agglomerate rearrangement.

Ideally, the breakpoint pressure will be taken as the relative estimate of the strength of granules. However, it was observed that there was no marked difference in the breakpoint pressure values of the different trials. It appeared that granules of the same size started crushing almost at the same point, regardless of granule strength. However, a distinct feature was apparent from the compression and crushing curve of harder granules. Generally, weak granules tend to break very rapidly and crushing and compression behavior linear portions in the curve slope sharply. In contrast, compaction of harder granules develop slopes leaning towards the horizontal direction. It is in this light that the criteria used for stronger granules were the lowest compression and crushing slopes relative to the values of the other trials. The slope of each compression and crushing curves were then determined and added together. The lowest total value formed the basis of comparison for this crushing strength test.

Results and Analysis

Crushing strength

Effect of fly ash The results of the crushing strength tests per granule will be discussed first. The effect of moisture content on the crushing strength of granules is illustrated in Figure 12. It does not include agglomerates derived from using 23% moisture content since it only resulted in caking in the pan and ending up with a big lump of solid material. The results clearly elucidates the extreme dependence of ball formation on moisture content. Using lower moisture for agglomeration caused poor particle adhesion and less durable agglomerates. The granules were sliding on the surface of the wall rather than rolling and this reduced the compaction forces acting on the granules. With increasing moisture, a

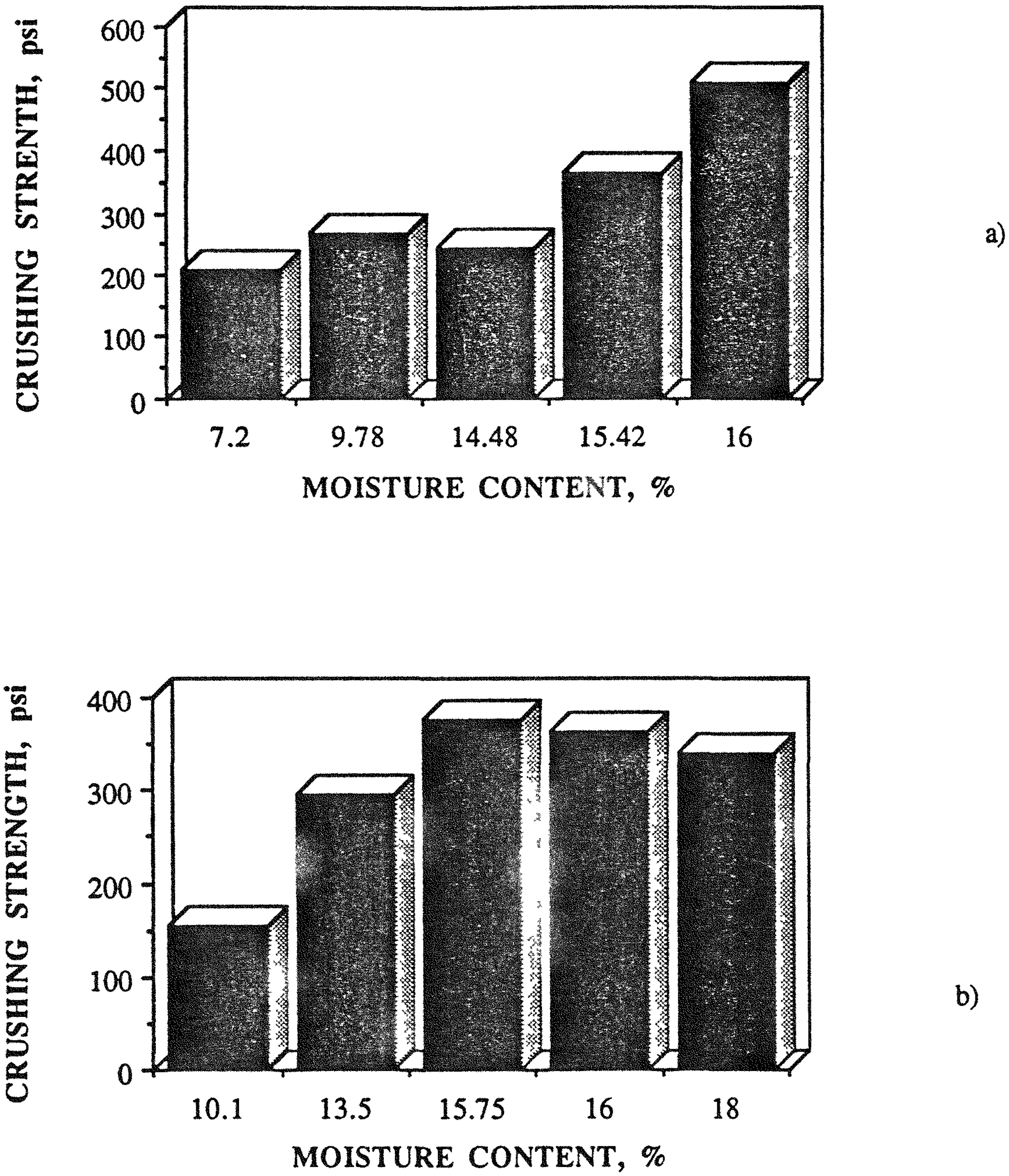


Figure 12 a. Effect of moisture content on the crushing strength of fly ash-sludge granules a) single agglomeration, b) double agglomeration more rapid growth formation and stronger granules were achieved[18,65]. This pattern is very evident in Fig.12a, where the optimum moisture content was around 16%. The double agglomeration supported this finding since optimum was maintained at 15-16 % moisture content. In excess of this critical moisture content, the granules showed signs of decreasing strength as seen in Figure 12b.

Figure 13 shows the effect of retention time on the strength of the granules. For single agglomeration, optimum retention time is three minutes Longer retention time of 4 and 5 minutes result in lower crushing strength which could be attributed to the breakage and abrasion of the newly formed granules. However, the granules prepared from longer retention times still exhibit greater strength than those produced from shorter periods (1 and 2 minutes.). On the other hand, the graph for double agglomeration reveals longer retention times (4 and 5 minutes) achieve greater densification , hence, stronger granules. It can be inferred from these findings that the dominant mechanisms of ball formation without the addition of fresh feed are breakage, layering, and coalescence of broken fragments. Sufficient time is required for compaction.

The optimum angular speed of the disc is 40 rpm for single agglomeration, as seen in Figure 14. A similar pattern can be observed from the crushing strength values of doubly-agglomerated granules. It suggests that a moderate speed of rotation is highly preferred over a faster speed for successful granulation . Too much mixing and agitation may result from operating at higher angular speed of the disc, leading to breakage and abrasion of the granules. This condition may be preferred for continuous operation but may prove detrimental in a batch system. Either 35 or 40 rpm can be adopted for single agglomeration and 30 or 40 rpm for double agglomeration.

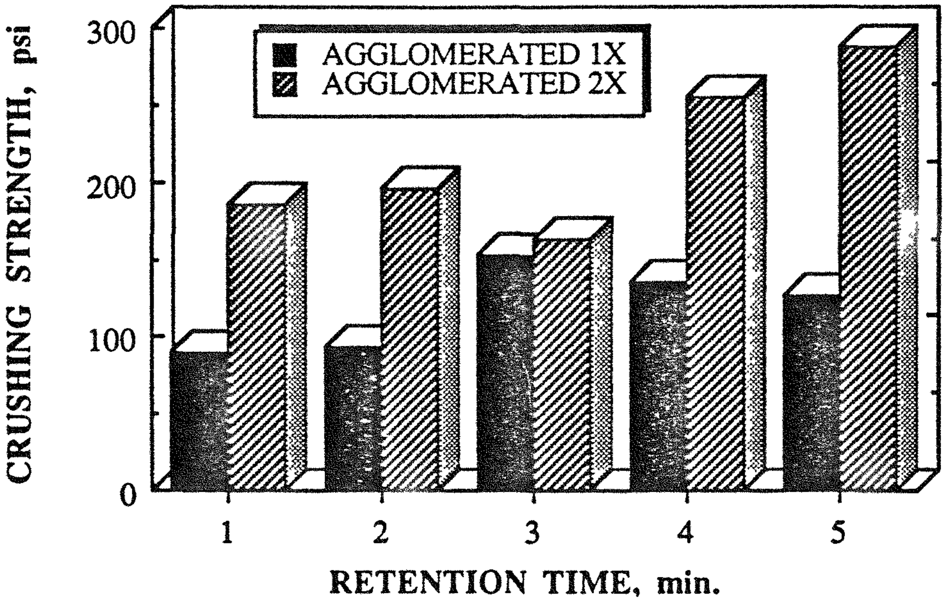


Figure 13. Effect of retention time on crushing strength of single - agglomerated fly ash-sludge granules

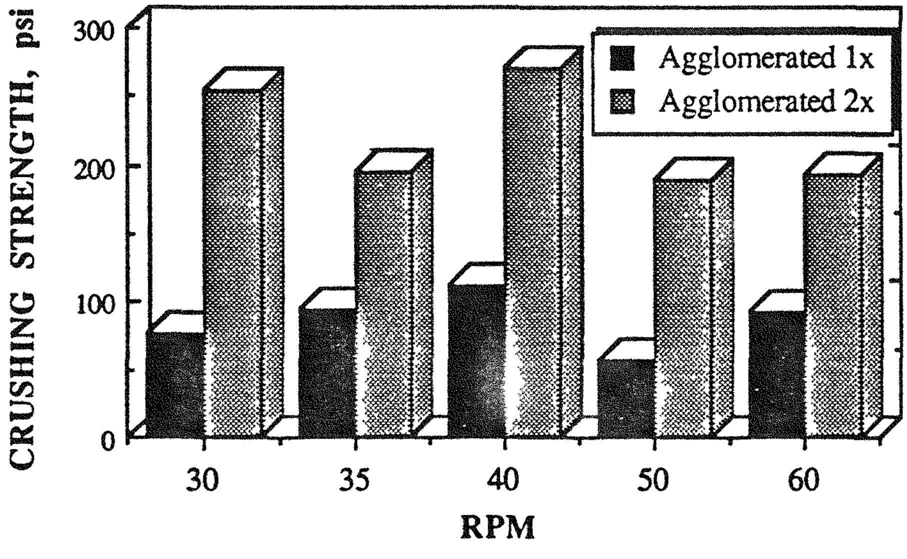


Figure 14. Effect of angular speed on crushing strength of double-agglomerated fly ash-sludge granules

Pressure-Density Compaction Test The simplicity of the test enabled the investigation of the effect of granule size on the optimum conditions of agglomeration. Two granule sizes were used, 1/2" and 3/8" but the test was restricted to products of first agglomeration only. These samples were used as models to determine the compatibility of the results of both testing procedures.

The plot of compacted bulk density and the applied pressure generated curves typical of the compaction behavior of aggregates systems. The slope of each portion were calculated and the sum of the slopes of compression and crushing lines were plotted as a function of the parameter being evaluated. The lowest sum value indicates the best condition.

Figure 15 shows the effect of moisture content in the compaction and crushing of the agglomerates. For a 3/8" size, optimum was confined in the area of 14.5-16% moisture content. Approximately 15-16 % moisture appeared to be the ideal condition for a 1/2" granule. A slight increase in moisture content with granule diameter is observed. The optimum values coincide with the results of the single granule crushing test.

The optimum retention time for 1/2" granules is three minutes as seen from Figure 16. Five minutes retention time for the same size also produced granules of high strength. These findings agree with previous results including the 4 and 5 minutes retention times forming stronger granules. The optimum retention time for the 3/8" size was found to be 2-3 minutes.

Figure 17 shows that the best angular speed for both sizes is 30 rpm. Based on single granule crushing test, the optimum for single agglomeration is 40 rpm. Actually, no pronounced difference was observed on their crushing strength values, 85 and 110 psi for 30 and 40 rpm, respectively. This part of the test gave inconclusive results. Therefore, an angular speed of 30 rpm seems reasonable.

The effect of feed rate on granule strength is illustrated in Figure 18. For a half inch diameter granule, 30-40 grams per minute produced relatively strong granules. On the other

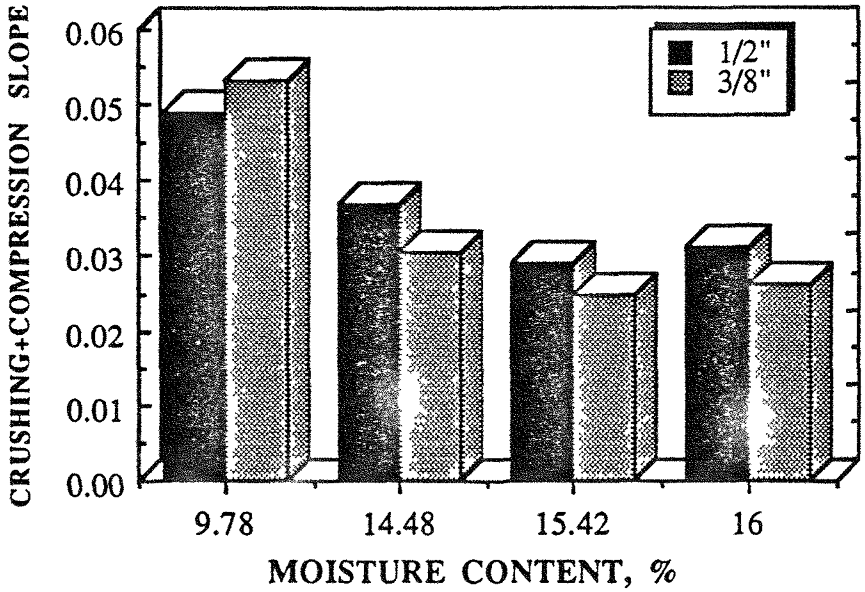


Figure 15. Effect of moisture content and granule size on pressure-density compaction of single-agglomerated fly ash-sludge granules

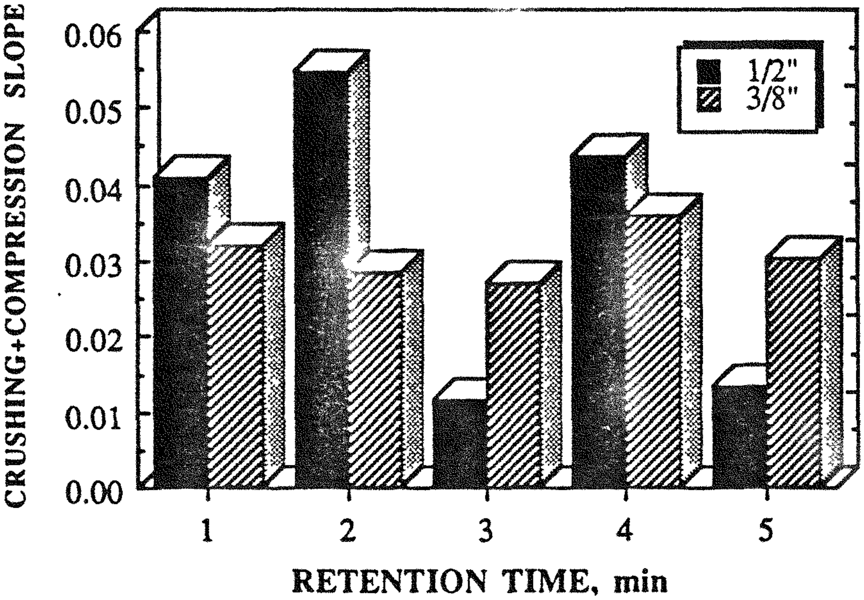


Figure 16. Effect of retention time and granule size on pressure-density compaction of single-agglomerated fly ash-sludge granules

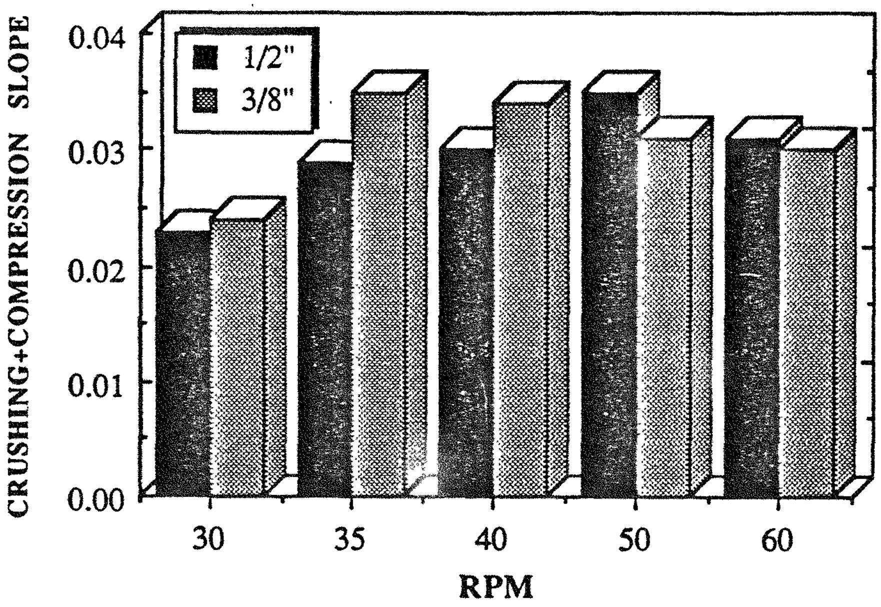


Figure 17. Effect of angular speed and granule size on pressure-density compaction of single-agglomerated fly ash - sludge granules

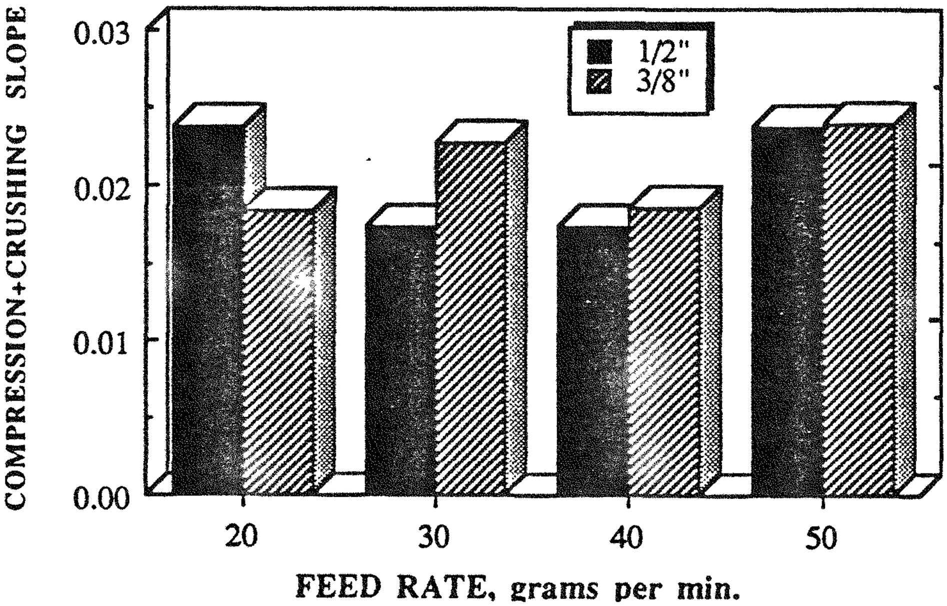


Figure 18. Effect of feed rate and granule size on pressure-density compaction of single-agglomerated fly ash-sludge granules

hand, 3/8 " size agglomerates were prepared best by using 20 or 40 grams per minute. A slower feed charge rate provides more time for compaction and layering during the ball growth process. It also provided more uniform layering since there was enough time for the granules to roll and complete one cycle. Furthermore, buildup of material on the walls of the agglomerator is minimized, if not eliminated.

In summary, the results of the pressure-compaction tests support those of the single granule crushing test for half-inch diameter granules. Granule durability apparently increases with granule diameter, from 3/8" to 1/2" size-granules, but only at the optimum conditions. Otherwise, the smaller granules exhibit higher physical integrity.

Effect of Kiln Dust Using kiln dust alone for solidification of the simulated sludge in the agglomeration process resulted in the failure of the granules. The hydration of lime caused expansion within the granule and possibly induced cracking in a manner similar to that of a hardened cement paste. Fractures may have initiated along the weakly bonded basal planes of $Ca(OH)_2$ and led to eventual disrupture of the granules.[66] Drying shrinkage due to loss of moisture on the surface may also have contributed to cracking. It is strongly believed by the author that a pressure gradient exists between the inner and surface layering of the granules. The difference in pressure is brought about by simultaneous occurrence of expansion and shrinkage phenomena on the inside and surface layer, respectively. The actual mechanism for this type of behavior is not clearly understood and is beyond the scope of the study.

Re-agglomeration proved to be a viable way of solving the cracking problem and produced granules with sufficient strength. Cracking was not observed in both inner and outer layering. This could be explained by assuming that both layers expanded at the same rate. Note that the hydration of fly ash produces ettringite which causes large volume increases. With a thicker outer layering due to double agglomeration, the effect of drying shrinkage may have been compensated by the expansion of ettringite. Results of the crushing strength tests are summarized in Figures 19, 20, and 21.

The effect of moisture content is clearly indicated in Figure 19 where significant gain in strength can be realized upon increasing moisture from 9.5 to 17%. The trend seems to indicate a slight increase from the 15-16% optimum moisture content of double agglomeration with fly ash. These results may imply that the amount of water required to give good adhesion and bonding is limited by the agglomeration process itself. Too much water results in caking and formation of lumps of solid material while a very small amount of water causes sliding of material and weak granules. The optimum moisture content was therefore within the range of 16-17 %.

Based on Figure 20 a retention time of three minutes produces granules of maximum strength. The same mechanisms observed in the agglomeration with fly ash predominate, that of abrasion transfer and breakage. Further granule compaction is achieved as they continue to roll and collide with each other. Afterwhich, the newly formed layers abrade and breakage of the weak granules eventually occurs. In this case, the optimun retention time was foundto be three minutes after the feed had been discharged into the pan.

Figure 21 clearly illustrates the importance of a slower speed of rotation in the process of agglomeration. Both 30 and 35 rpm gives relatively higher strength values as opposed to those produced from 40-50 rpm. The optimum is at an angular speed of 35 rpm which is in agreement with the previous trials.

There appears to be a contradiction in the strength values of agglomerates with and without kiln dust. Inclusion of lime, in the form of kiln dust, was expected to provide additional strength to the granules, however, the opposite was realized. Several reasons may be advanced to explain this behavior. For example, immediate setting of the waste may have transpired, using all free water and leaving none for subsequent pozzolanic reactions.

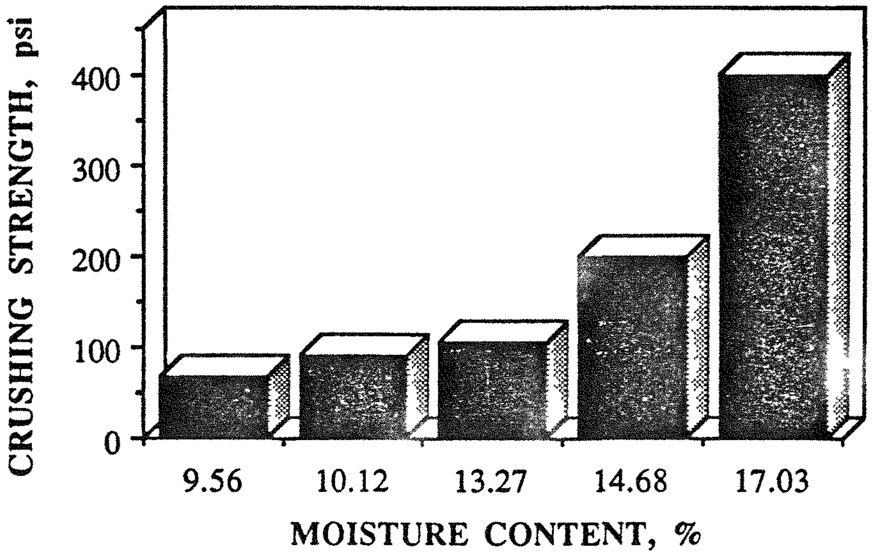


Figure 19. Effect of moisture content on crushing strength of granules using kiln dust

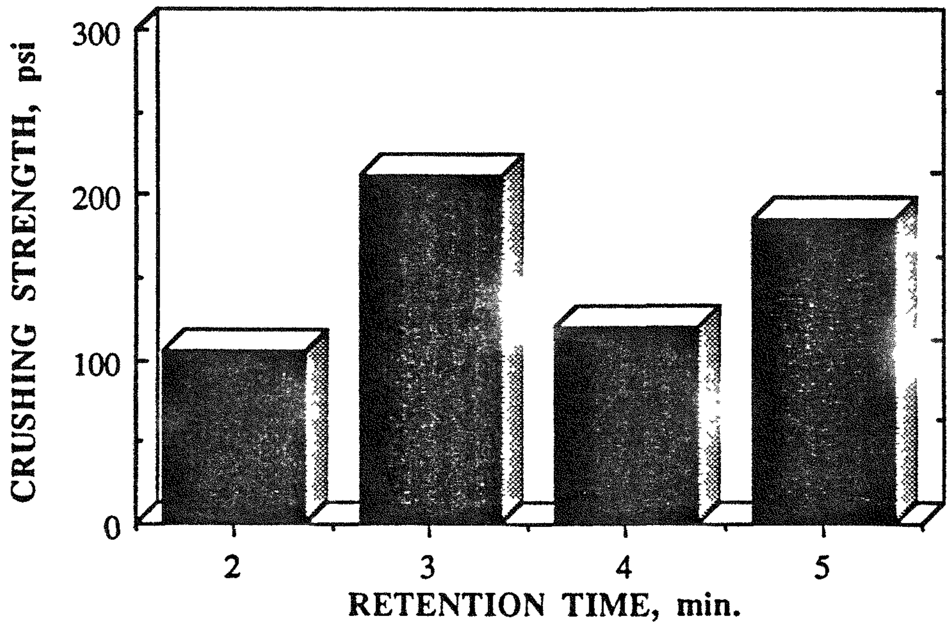


Fig.20. Effect of retention time on crushing strength of granules containing kiln dust

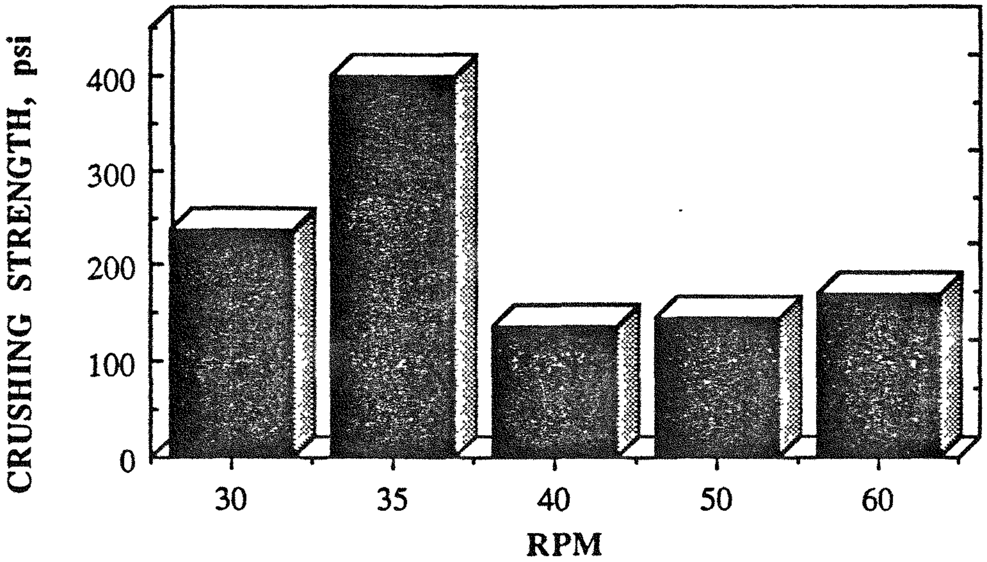
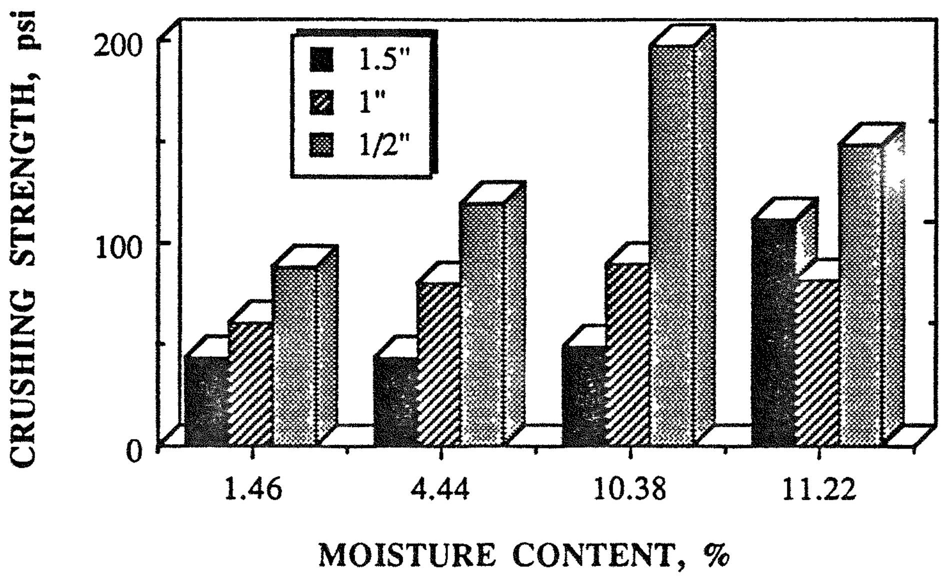


Figure 21. Effect of angular speed on crushing strength of granule containing kiln dust

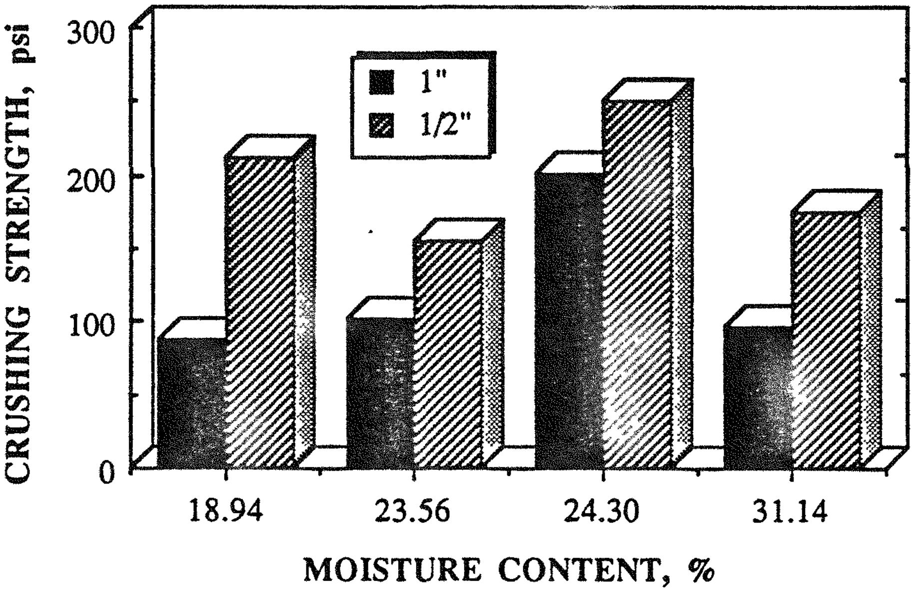
Consequently, the granules became friable due to the unreacted components in the structure.[45] The presence of calcium hydroxide plates in the matrix may also have caused massive expansion thereby, creating internal flaws in the structure. Furthermore, stacked shells of calcium hydroxide crystals may have formed around some of the fly ash spheres resulting in very slow diffusion of water for significant hydration to occur.

Since previous results indicate complete agreement of the two crushing strength tests, as far as establishing the trend is concerned, the pressure-density compaction test was not performed for these granules. .

The results of trial 9 are presented in Figures 22a and 22b. Apparently, the amount of moisture required to give maximum strength was reduced as the proportion of cement kiln dust in the solidification stage was lowered. Approximately, 10-11% moisture by weight of fly ash was the optimum for single agglomeration of half-inch diameter granules. In the case of doubly-agglomerated samples, moisture content had risen to 18-24% for maximum strength of the granules. The sudden shift in optimum moisture content may be explained in terms of the



a)



b)

Figure 22. Effect of moisture content and granule size on crushing strength of sludge agglomerates containing 30% kiln dust a) single agglomeration, b) double-agglomeration

diffusion-controlled dissolution reactions in lime-high calcium fly ash systems. Calcium hydroxide crystals formed around the fly ash spheres may have retarded the diffusion of water through the membrane. Consequently, some water molecules were left in the pore solution to react with the available fly ash grains and caused a reduction in the amount of moisture required for agglomeration. However, the increase in moisture content for the second agglomeration only reinforces the theory of incomplete hydration reaction in the first stage of agglomeration. Water could have been adsorbed from the outer layers to continue the pozzolanic reactions in the system.

Significant reduction in durability with increasing granule diameter is very visible from the graphs of both single- and double-agglomerations. A slight improvement in durability was realized in decreasing the proportion of kiln dust in the granules, compared to the strength of the granules with either pure fly ash or kiln dust . The combined effect of these two cementitious materials enhances physical integrity of the granules.

The optimum moisture content of the agglomerates appears to be unchanged regardless of granule size. This supports earlier suggestion of an optimum moisture range effective for agglomeration.

Leachate Characteristics

Table 5 summarizes the results of Toxicity Characteristics Leaching Procedure (TCLP) for the simulated sludge. The analyses were carried out using EPA Method 1310 for copper, zinc, and nickel. Recommended maximum allowable limits are 500 ppm for zinc, 100 ppm for copper, and 200 ppm for nickel. This is based on the assumption by EPA that these leached heavy metals are diluted by a factor of 100 upon reaching groundwater.

As previously reported, the initial concentrations of zinc, copper, and nickel in trial 4 and 5 simulated sludges were 8000 ppm, 2700 ppm, and 3354 ppm respectively. The results are well below the level of concern and indicates that fly ash and kiln dust are effective stabilizing agents for use in the treatment of waste. Single agglomeration appears adequate in the immobilization of heavy metals and the results are comparable to those of double agglomeration. This strongly suggests the exclusion of re-agglomeration step in the treatment of this waste.

Table 5. Leachability of Agglomerated Simulated Sludge

	Cu (ppm)	Zn (ppm)	Ni (ppm)
Trial 4 - S.sludge particulated w/F.A.	0.085	0.097	0.831
Trial 4 - Double Agglomeration	0.058	0.088	0.124
Trial 5 - S. Sludge particulated w/K.D.	2.077	4.364	0.227
Trial 5 - Single Agglomeration	0.268	0.641	0.323
Trial 5 - Double Agglomeration	0.066	0.030	0.224

X-ray diffraction

The bulk mineralogy of singly-agglomerated simulated sludge consists of ettringite, quartz, and periclase. Strong peaks for these compounds are evident in Figure 23. Ettringite is a typical hydration product of fly ash; and quartz and periclase (MgO) exist in most fly ash systems.

In order to gain a deeper insight into the cracking phenomenon when using kiln dust as solidifying agent, the particulated sludge was analyzed using XRD. Figure 24 shows quartz, gypsum, illite, albite, and possibly calcium zinc hydroxide hydrate and zapatalite in the pattern.

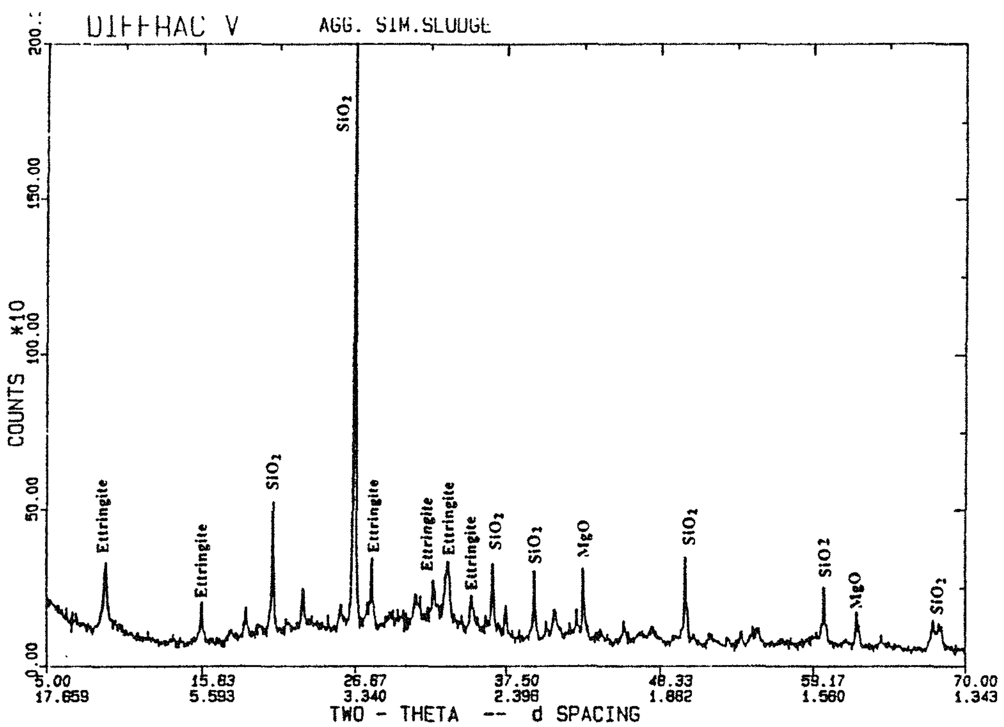


Figure 23. X-ray diffractogram of single-agglomerated simulated sludge using Lansing fly ash

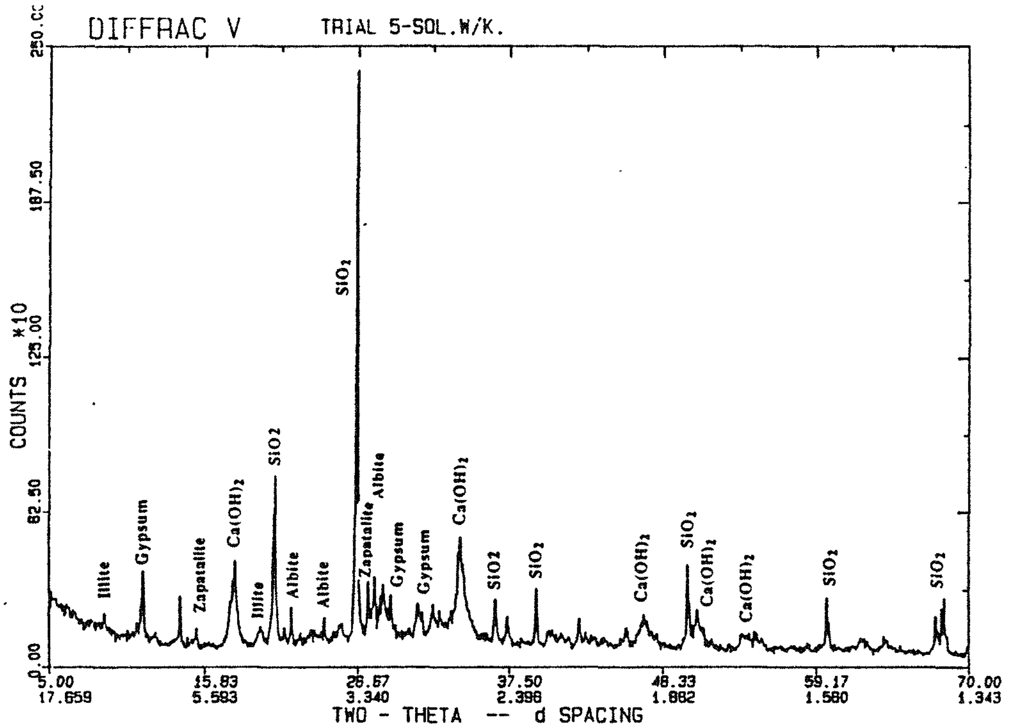


Figure 24. X-ray diffractogram of solidified simulated sludge with kiln dust

Of particular interest is the strong presence of calcium hydroxide which supports the earlier suggestion of an expansion theory. This implies that there is a maximum percentage of lime that can be used beneficially for agglomeration purposes.

Scanning Electron Microscopy

Examination of the microstructure of Trials 4 and 5 showed distinct layers in single and double agglomeration. Figures 25 and 26 illustrate the continuous network formed during the hydration of fly ash. A less porous structure is observed in the outer layers compared to the inner kernel. This effect is observed to a greater extent in sludge particles agglomerated with kiln dust. The solid chunk noticeable on the boundary between the inner kernel and first layer in Figure 26 is a calcium-silica rich soil aggregate. This strongly points out the breakage into smaller fragments and subsequent coalescence during the agglomeration process. The layers also emphasize the snowballing effect as the granules continually grow in size. The discontinuous lines were developed when the granules were cracked open for microscopic analysis.

A closer investigation on the sludge agglomerated with kiln dust on Figure 27 reveals the presence of calcium hydroxide plates and reacted soil minerals. No spherical particles are observed from the picture, only aggregated particles. The void spaces were the effect of inadequate compaction. In contrast, the photomicrograph of a small hole in the simulated sludge particulated with fly ash is presented in Figure 28. Clusters of needlelike structures identified as ettringites have precipitated underneath the exposed surface. This only confirms the XRD findings.

Figure 25. Single-agglomeration of simulated sludge with fly ash showing layers formed and an intact inner kernel

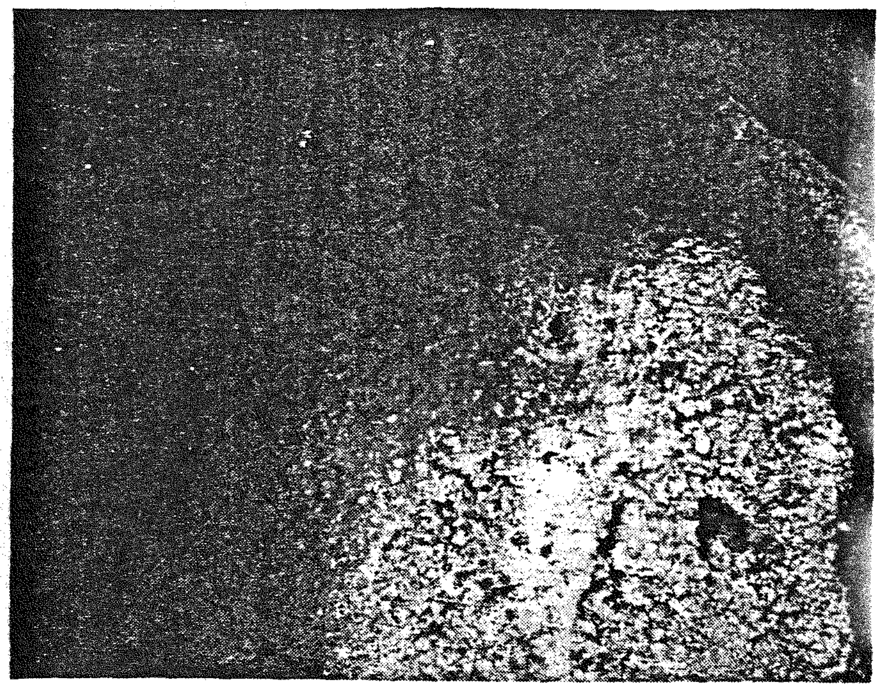


Figure 26. Double-agglomeration of simulated sludge with fly ash showing formation of layers

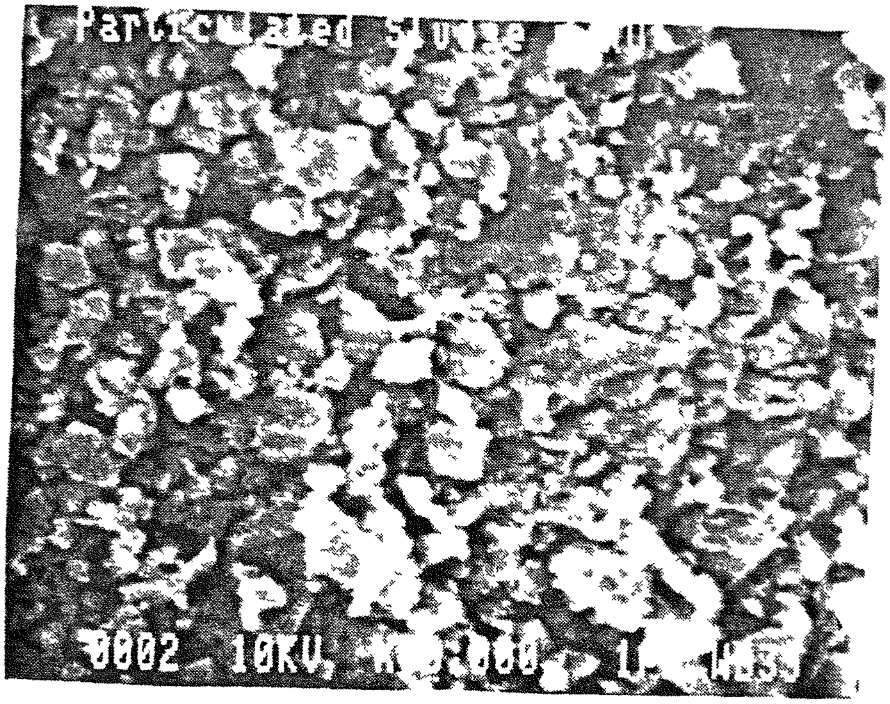


Figure 27. Simulated sludge solidified with kiln dust

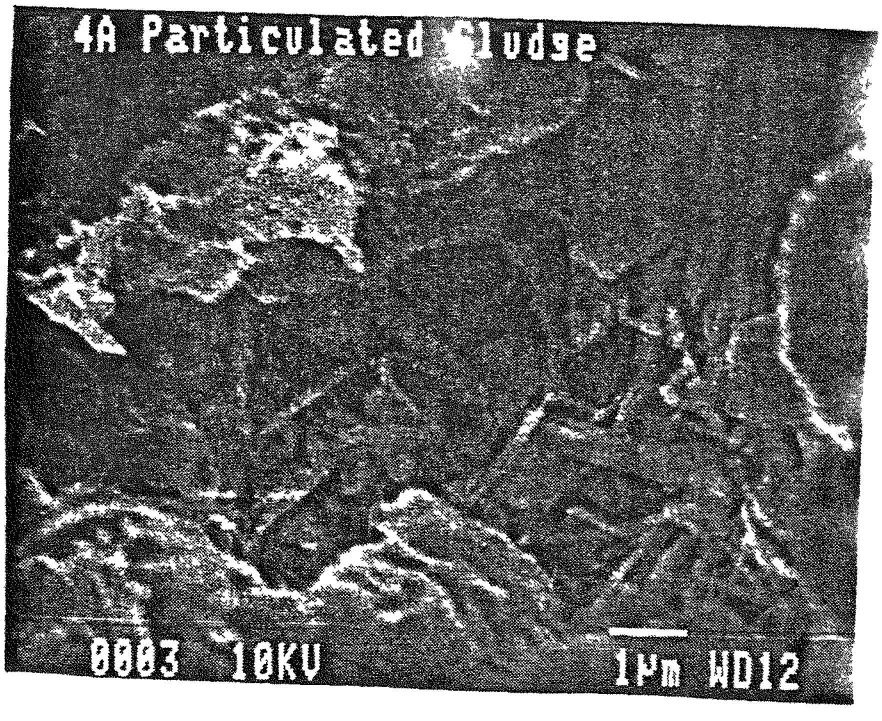


Figure 28. Exposed zone of agglomerated simulated sludge solidified with fly ash

Conclusion

The trials carried out using the simulated sludge have a twofold advantage. First, they strongly provided the basis for using fly ash as an effective stabilizing agent in the treatment of waste. Immobilization of metal compounds appears to have been successful, as reflected from the TCLP results. Incorporation of high calcium fly ash results in an alkaline solution favorable for the transformation of heavy metal salts into some hydroxide compounds. Metals salts are highly soluble in water and therefore exist as ionic species in solution. In the presence of hydrated lime from fly ash, precipitation of the hydroxide compounds is highly favored, with solubility product constants at 25°C in the lower range of 10^{-17} and 10^{-16} for zinc and nickel hydroxides, respectively.[67] Unfortunately, most metal hydroxides exist in amorphous forms difficult to detect by x-ray diffraction techniques which may explain their absence from the patterns. These metal hydroxides are highly insoluble in water or in slightly acidic environment. Therefore a possible immobilization mechanism may be exchange of base ions in the conversion of these metal salts into stable compounds. A third possibility is the formation of hydration products which cause entrapment of the contaminant within the crystalline structure. It may also be possible that all mechanisms have occured simultaneously with the net effect of entrapment of the contaminants.

Another likely possibility of containment is the interaction between metal salts and clay minerals available from the soil itself. Muscovite is a prototype mica mineral for illite with a chemical formula of $KAl_2[AlSi_3O_{10}](OH)_2$.[68] It is a dioctahedral mineral, with two aluminum atoms in the octahedral sheet. One aluminum atom substitutes for one of the four silicon atoms in the tetrahedral sheet and the charge deficiency is balanced by potassium cations in between the closely stacked sheets or in the holes in the adjacent silicone layer.[69] The illites are derived from this prototype by variations in both the tetrahedral and octahedral substitution, resulting in a total net negative lattice charge. Adsorption of cationic metals such as zinc, copper, and chromium (III) is greatly enhanced with an increase in pH made possible by fly ash addition.[45] The negative surface charge of the clay structure cause a non-reversible adsorption which can be more appropriately termed as chemisorption.[45] The latter has binding forces greater than those of pure adsorption but should not be taken as true chemical bond. At this point, only suppositions can be given on the actual mechanism of fixation. However, one can say with assurance that the degree of protection to the environment is intensified by the structural integrity of the granules.

The influence of cement kiln dust on the overall quality of the granules was also investigated. There is evidence to prove that a reduction in the proportion of kiln dust in the agglomerates resulted in a slight improvement of granule durability. There appears to be an optimum proportion of kiln dust benefecial for the agglomeration of simulated sludge with fly ash. Further investigation of this problem was carried out in the next phase of the study.

The second benefit derived from these experiments is the determination of the optimum conditions for agglomeration of the electroplating sludge. Based on these experiments, agglomeration of metal-rich sludge with fly ash can be best achieved using a moisture content of 14-16 % by weight of fly ash, an angular speed of 30 rpm, and a retention time of 3 minutes. Inclusion of kiln dust did not alter the operating conditions very much. Optimum moisture was found to be within 15-17% by weight of fly ash, an angular speed of 35 rpm, and retention time of 3 minutes. These results are for granules produced from single agglomeration. Leaching results proved to be very encouraging even for single agglomeration. Consequently, in order to maximize the use of materials resources and consumption of energy, single agglomeration would only be considered for the next phase of the experiment.

PHASE II. AGGLOMERATION OF ELECTROPLATING SLUDGE

Agglomeration of the electroplating sludge was accomplished with and without the preconditioning step as practised in the first phase of the experiment. Preconditioning referred to rehydration of the sludge, followed by solidification using fly ash-kiln dust mixture. The importance of preconditioning as an integral part of sludge preparation for agglomeration was evaluated. Studies indicate that the extra water for absorption should be added ahead of time in order to utilize the granulator to the fullest extent capacity.[11] In this way, time and granulator space are not wasted to allow for absorption to occur. However, the electroplating sludge had a 40% moisture content which may be adequate in starting the seed pellets for agglomeration with fly ash. Preliminary testing was conducted to investigate the feasibility of using the electroplating sludge in its "as received" state of moisture content. The rationale was to maximize all possibilities for pan agglomeration in the most viable, economical, and simple manner.

Preliminary Testing

In order to illustrate the effect of variation of the cementing properties of two fly ashes, agglomeration of the electroplating sludge was performed using Lansing and Ottumwa fly ashes. The sludge was prepared by sieving and grinding to the desired fineness prior to agglomeration, after which, a known amount of sludge was charged directly into the pan. Mixing and agglomeration with fly ash occured simultaneously while regulating the feed rate at 30 grams per minute and keeping moisture content at 14-16%. Agglomeration was performed using 25, 50, and 75% sludge by weight of total mixture. The granules produced at this point demonstrated weak physical integrity and required a second agglomeration to improve granule strength.

The durability of the granules was evaluated using crushing strength test and the results are presented in Figure 29. The effect of fly ash type on granule strength as seen in the figure is expected, with agglomerates made from Lansing fly ash showing higher strength. In addition, granules with 25% sludge are far superior in strength than those prepared using higher proportion of sludge in the mix. Little variation in strength is exhibited by both granules containing 50 and 75% sludge.

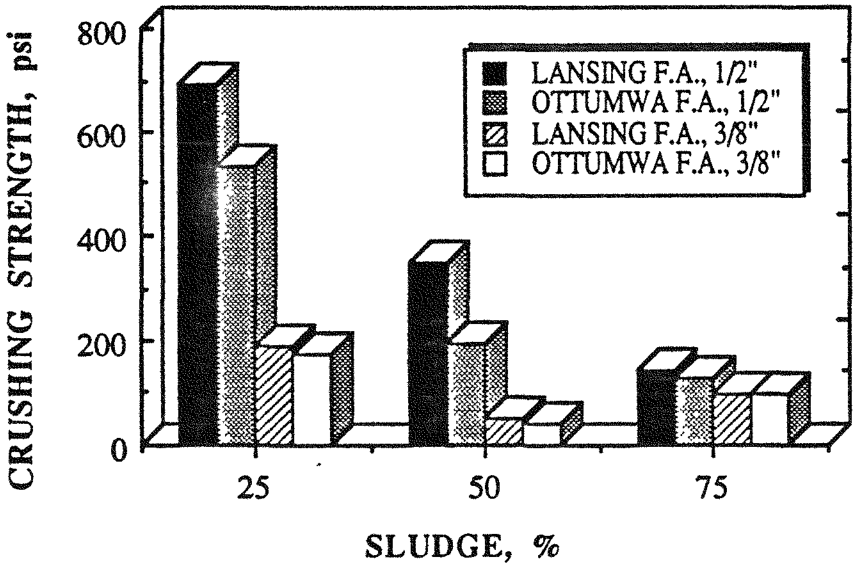


Figure 29. Effect of fly ash type and sludge proportion on the crushing strength of granules

Leachate tests have been carried out for double-agglomerated granules in accordance with federal regulations. The results are summarized in Table 6. With the leachate concentration well below the level of concern, it clearly indicates the effectiveness of using fly ash in immobilizing heavy metals. Note that the original concentrations of copper, zinc, and

Table 6. Leachability characteristics of agglomerated electroplating sludge

	Lansing		Ottumwa		Det. Limit (mg/L)	Max. Conc. (mg/L)
	50% Sludge (mg/L)	75% Sludge (mg/L)	50% Sludge (mg/L)	75% Sludge (mg/L)		
Zn	0.593	0.371	29.753	40.953	0.002	500
Ni	0.887	0.685	6.484	7.084	0.05	200
Cu	0.056	0.065	0.237	0.353	0.003	100
As*	< 1.4	< 1.4	< 1.4	< 1.4	< 1.4	5
Ba	< 0.5	< 0.5	< 0.4	< 0.4	0.2	100
Cd	<0.002	<0.002	<0.01	< 0.01	0.002	1
Cr	0.55	0.58	0.28	0.27	0.002	5
Pb	< 0.01	< 0.01	< 0.01	< 0.01	0.01	5
Hg*	< 9	< 9	< 9	< 9	9	0.2
Se*	3.9	3.9	6.1	4.8	0.5	1
Ag	<0.005	<0.003	<0.002	<0.012	0.002	5

*Note that leachate concentrations for As, Se, and Hg are expressed in µg/L. All other results, detection limits, and maximum concentration are expressed in mg/L.

nickel in the sludge were 7700, 117, 700, and 42, 400 ppm respectively (as reported in Table 4). A comparison of Lansing and Ottumwa fly ashes shows Lansing to exhibit better stabilizing capability. This is in agreement with previous results whereby the cementing properties of Lansing fly ash have been found to be superior to Ottumwa fly ash. Small variation in the leachate potential of the agglomerates made form Lansing fly ash is evident. On the other hand, agglomerates made from Ottumwa fly ash showed a considerable increase in leachate concentration especially the zinc concentrations. This further illustrates the superiority of Lansing fly ash in terms of cementing properties.

Recent studies have emphasized the role of fly ash hydration products, particularly ettringite, in the fixation of hazardous compounds.[70] Ettringite is a calcium aluminosulfate hydroxide hydrate [$Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$] formed from the reaction of tricalcium aluminate (C_3A) with water in the presence of sulfate ions.[33] Apparently, partial or complete substitution between ions of same sizes and charges occurs and ettringite does not have the exact stoichiometry as denoted previously. It is commonly designated as the AFt phase for a series of chemically analogous isostructural compounds.[66] The XRD patterns shown in Figure 30 suggests the existence of a similar AFt phase. Bentorite is a chrome substituted ettringite which may be present in the granules made from 75% electroplating sludge. This reaction product is not improbable due to high chrome concentration in the sludge. A slight shift in the bentorite peaks from those of ettringite can also be observed. With respect to radii size, Al^{+3} measures 0.05 and chrome has 0.069 and same charge. The pattern also indicated a form of sodium zinc sulfate compound [$(Na_{0.9}Zn0_{.05})_2SO_4$]. A more detailed discussion of the possible mechanisms of fixation is provided in the next chapter.

In support of this observation, photomicrographic analysis was performed on the same samples. Energy dispersive x-ray analysis (EDXA) was utilized to help identify elements present in the needle-like structures of ettringite. Figure 31 shows the energy spectrum collected at a preset time of 100 seconds. Gold was present because it was used to coat the samples. An appreciable amount of chrome can be detected from the pattern. The relative intensity of the peaks shows the relative amount of chrome and aluminum. and indicates the presence of more chrome than aluminum. However, it should be emphasized that the spectrum might have proportionalities which differ from their elemental concentration.[43] X-ray signals obtained for different elements depend not only on the concentration but also on the binding energy of the K-shell electron of the concerned element. Nevertheless, the analysis indicates that it has more chrome than aluminum present in the ettringite crystals.

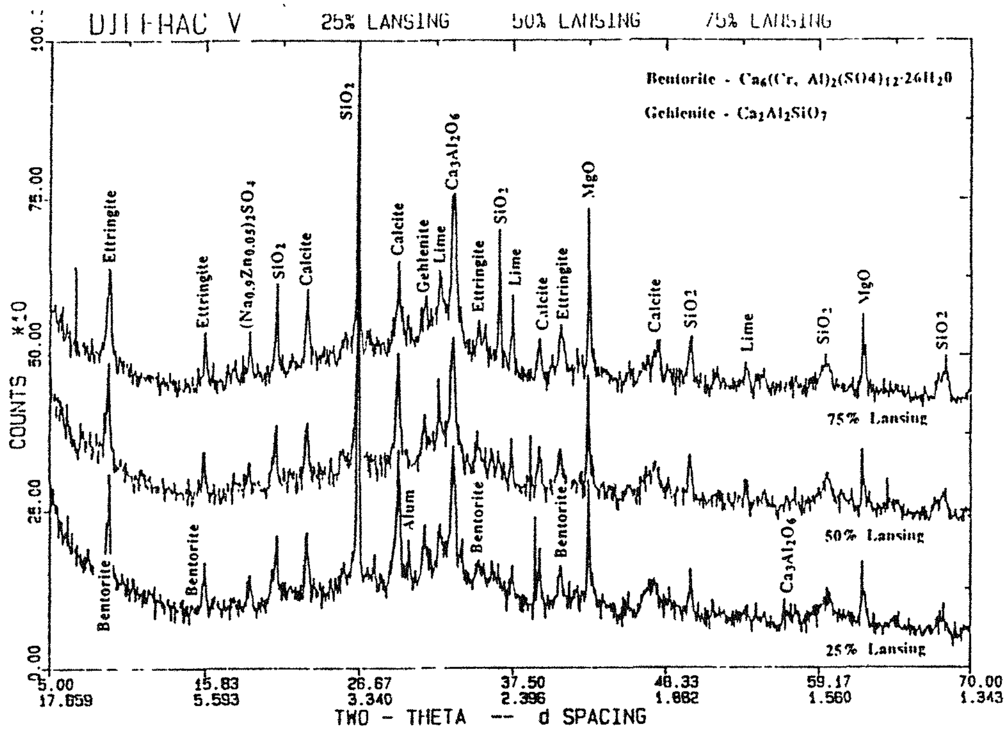


Figure 30. X-ray diffractogram of agglomerated electroplating sludge

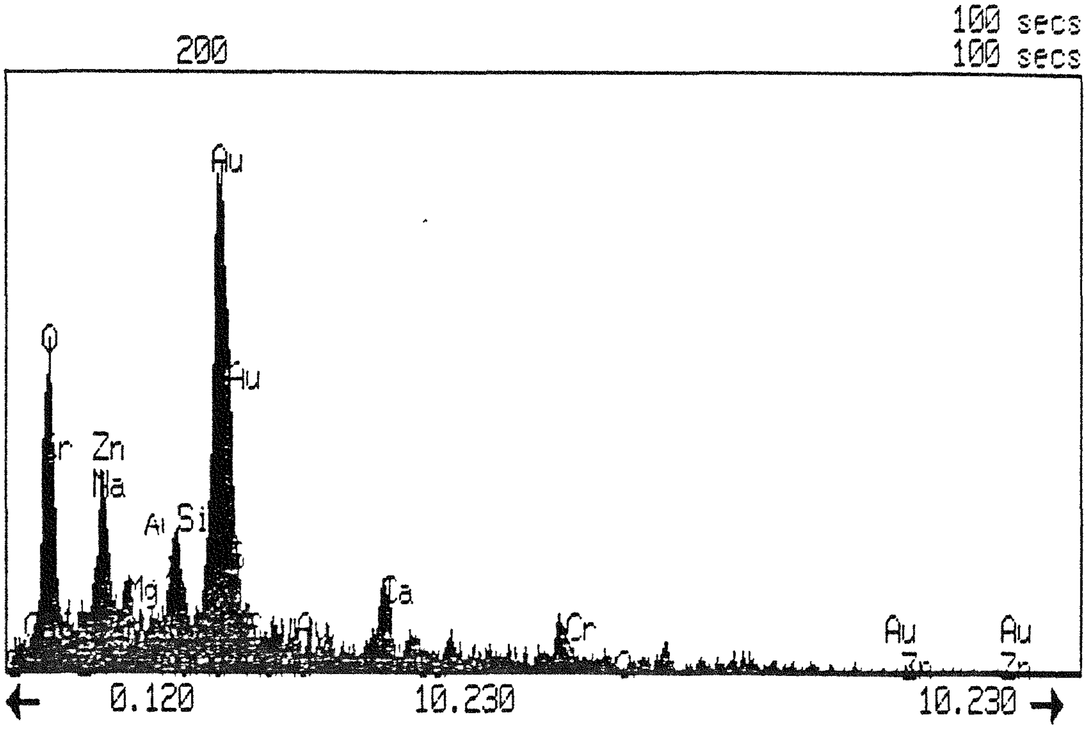


Figure 31. Energy dispersive x-ray analysis of agglomerated electroplating sludge

Sludge Preconditioning

Agglomeration of electroplating sludge without preconditioning required a second layering of fly ash. Particles of sludge did not appear to be deeply embedded in the hardened fly ash paste as opposed to the agglomerated simulated sludge. Double agglomeration proved to be benefecial in terms of strength, however the structural integrity of the granules needed improvement. Other aspects of the procedure have to be considered such as increase in materials and operating expenses. The time for agglomerating a batch of sludge also became longer, since single agglomeration takes from 30 minutes to 1 hour. Therefore, a second alternative was developed which involved preconditioning the sludge with fly ash and kiln dust. According to the simulated sludge experiments, the total moisture content at the end of preconditioning was approximately 26% . The flow scheme from Phase I was adopted and is outlined in Figure 32. The preconditioning experiments were carried out with Lansing fly ash.

Effect of kiln dust

The groundwork for using kiln dust as a stabilizing agent had been initiated in the first phase of the study. Based on the results, the proportion of kiln dust had to be lowered in order to prevent the adverse effect of cracking. The best conditions for the formation of good quality granules were also established from the crushing strength test results derived from the study. The main objective of this investigation was to find the percentage of kiln dust which would give maximum benefits, in terms of stabilization and strength.

Mixtures of fly ash, sludge, and kiln dust were prepared for agglomeration. The samples prepared, with the corresponding codes, were:

a) 1:1 Sludge : Fly Ash --> 1:1 SL:FA

b) 1:2 Sludge : Fly Ash --> 0% K.D.

c) 1:2 Sludge : Fly Ash + 5% Kiln Dust --> 5% K.D.

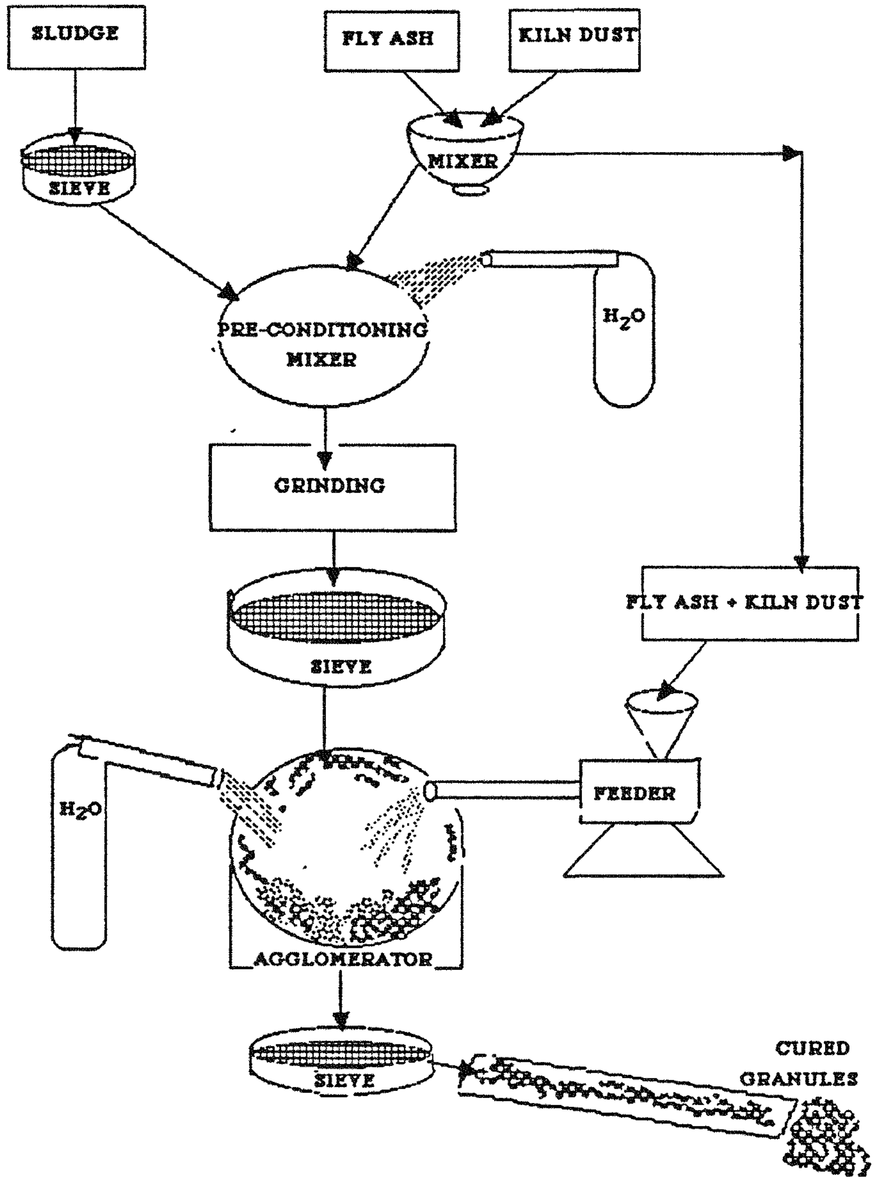


Figure 32. Flow scheme of agglomerating the electroplating sludge using high calcium fly ash and cement kiln dust

d) 1:2 Sludge : Fly Ash + 10% Kiln Dust --> 10% K.D.

e) 1:1 Sludge : Fly Ash + 20% Kiln Dust --> 1:1SL:FA+20% K.D.

f) 1:2 Sludge : Fly Ash + 20% Kiln Dust --> 20% K.D.

The sample codes will be sometimes referred to in the text . Unless otherwise noted, the proportion of the sludge and fly ash-kiln dust refers to 1:2 ratio with the corresponding percentage kiln dust used. The agglomerates mentioned shall always be taken to contain the electroplating sludge, unless stated otherwise.

Water was added to rehydrate the sludge and bring the total moisture content to 60% prior to solidification . Five hundred grams of this preconditioned sludge were allowed to agglomerate for five minutes in order to maintain homogeneity of the composite granules. Instead of the customary procedure of incorporating kiln dust only in the solidification stage, different proportions of kiln dust were mixed with fly ash for layering/agglomeration of the granules. Kiln dust was varied from 0, 5, 10, and 20% by weight of the fly ash mixture. A parallel study on the effects of kiln dust on the outer layers of the granules was also investigated. Consequently, mixtures of 5 and 10% kiln dust in the solidification stage were prepared and agglomerated using only fly ash. The same ratio of 1:2 sludge:fly ash-kiln dust was adopted for the solidified sludge. The agglomerates therefore have a pure fly ash layering with an inner kernel that contains either 5 or 10% kiln dust. These samples shall be described when referred to in order to avoid confusion with the other 5% and 10% kiln dust samples.

The proportions of preconditioned sludge for agglomeration were also varied. Agglomeration proceeded using equal amounts of solidified sludge and fly ash-kiln dust . The compositions of the agglomerates were altered from the 25 - 75 % range used in the preliminary testings. Maximum utilization of the electroplating sludge waste without sacrificing the quality of the granules was evaluated.

Effect of Curing

In order to evaluate the importance of curing on the strength formation of the agglomerates, samples were prepared according to the procedures outlined previously. However, the investigation was restricted to using a 1:1 ratio of sludge to fly ash-kiln dust mixture. This would emphasize the difference between air-cured (A.C.) and humidity-cured (H.C.) granules. The samples prepared for agglomeration were:

a) 1:1 Sludge : Fly Ash (A.C.) --> 1:1 SL:FA (A.C.)
b) 1:1 Sludge : Fly Ash (H.C.) --> 1:1 SL:FA (H.C.)
c) 1:1 Sludge : Fly Ash + 20% Kiln Dust (A.C.) --> 1:1 SL:FA+20% K.D.(A.C.)
d) 1:1 Sludge : Fly Ash + 20% Kiln Dust (H.C.) --> 1:1 SL:FA+20% K.D.(H.C.)

Evaluation of Granule Properties

Information on the basic characteristics of the agglomerates are necessary to evaluate the degree of fixation in the agglomeration of the metal-rich sludge waste. The physico-chemical properties were determined using modified versions of the standard testing procedures, taking advantage of the available equipment in the laboratory.

Physical properties

Physical durability of the granules was measured based on the following parameters: crushing strength, freeze-thaw resistance, abrasion resistance, porosity, specific gravity, and absorption. With the exception of porosity, specific gravity, and absorption, modifications to the standard testing procedures were developed to suit the limited quantity of the samples. The pressure-density compaction test, which had been discussed in an earlier section, was used to measure crushing strength of the granules.

The tests were performed on granules 3/8"-1/2" in size and cured for 28 days. In cases where there was sufficient sample, a gradation was established in order to evaluate their potential as aggregates. The gradation requirements for coarse aggregates intended for portland cement concrete was adopted according to ASTM C33 for a 3/4" - #8 size range. Table 7 summarizes the sample gradations used for abrasion and free-thaw tests and the corresponding ASTM gradation requirement.

Table 7. Gradation requirements adopted for abrasion and freeze-thaw tests showing percentage passing

	1"	3/4"	1/2"	3/8"	#4	#8
ASTM C33	50-100	30-100	20-75	5-55	0-10	0-5
Abrasion	100	90	40	20	0	0
Freeze-Thaw	100	80-100	45-60	25-30	0	0

Porosity Pore structure was evaluated on half-inch granules using a Quantachrome Autoscan 60-mercury porosimeter, capable of applying pressures up to 60, 000 psi. Force application to cause intrusion of mercury into the pores of the granules were broken down into three successive steps. The first was from 0-1200 psi, the second was ran from 0-6000 psi, and finally from 0-60, 000 psi. All data points were merged to give a continuous intrusion curve. Integration of the three different curves is possible for intrusion data only.

The surface tension and contact angle of mercury are taken as 480 erg/cm and 140.0 degree respectively.[3] The contact angle was based on that of portland cement.[71]

Specific Gravity The density and absorption of the granules were initially determined according to ASTM C 127-84 specifications. However, the reactivity of fly ash with water may have introduced errors in the calculations and results may not be accurate. The multipycnometer was also employed in measuring the true volume of the solid material. It uses helium gas to penetrate the finest pores and crevices approaching one Å to assure maximum accuracy.

Freeze-Thaw Resistance Test Method No. Iowa 211-A, Method C was used to determine the weathering resistance of the agglomerates. Instead of vacuum saturation, the samples were immersed in a water bath for 24 hours. The same samples were then placed in pans with water maintained half an inch above the surface. A control beam was used to regulate the temperatures of the freezer chamber. Thawing was provided by hot plates at the sides of the pans and signaled the end of one cycle. The method was completed after 25 cycles and the samples were collected and dried in the oven overnight. Sieving followed using the same mesh sieve sizes in building up the samples, plus the #8 sieve. The percent passing the #8 sieve was computed to a clean oven dry weight basis as the loss in the freezing and thawing test. High percentage loss indicates poor resistance to severe weather changes.

Abrasion Resistance Approximately 5000 grams of sample are required for one run of the L. A. Abrasion test. Due to the nature of the waste, a simpler and easier version was adopted to characterize the durability of granules. Portable roller mills and a cylindrical jar were used as the abrasion testing machine. The jar for the mill was made from porcelain fortified with Burundum ceramic material for increased resistance to wear.[72] It has a total capacity of 5 liters with a mouth opening of 133 mm, an inside diameter of 229 mm, and height of 292 mm. The samples were introduced in one end which was then tightly closed by a suitable, dust-tight cover bolted in place. The apparatus was mounted on two rubber rollers which automatically keep the jar in the center and rotated with the axis in a horizontal position. A controlled peripheral speed was furnished by a variable transformer to prevent the sliding and slipping actions of the granules. The abrasive charge consisted of twenty 1.9 cm. diameter steel spheres. In place of a prescribed number of revolutions to complete one test, the samples were ran for a period of five hours. On completion of the test, the materials were discharged from the machine and separated according to sieve sizes with the addition of #12 mesh size. The difference between the original weight and the amount retained on #12 sieve, in an oven dry basis, of the test sample is reported as the percentage wear. High percentage wear means that the aggregates may not be able to withstand the rigours of shipping and handling involved in the processing and disposal of the final products.

Chemical Properties

The physical changes accompanying granule formation can be interpreted in terms of the chemical changes that occured within the system. The morphology of the granules were examined using scanning electron microscope (SEM). Leachability tests were carried out, again conforming to the standard TCLP methods. However, the current TCLP test does not actually simulate any real world set of conditions but demonstrate a worst scenario for leaching. In principle, the leaching medium should be that which is actually in contact with the waste in the landfill. This is impossible to attain in a laboratory developed leaching test due to changes in composition with time. Recognizing these limitations, a short-term leaching test was developed using water as leaching medium.

Selection of water as leachant was made on the basis of recent studies on the solubility of these heavy metal compounds in a slightly acidic environment.[45,73] This is especially important for heavy metals that exhibit amphoterism, such as chromium, zinc, cadmium, lead, and arsenic. Amphoterism refers to a compound that can be both an acid or a base. Metal hydroxides of these compounds exhibit minimum solubility within the narrow range pH range of 7.5-10. Solubility increases rapidly with either an increase or decrease on both end limits of pH range. Therefore, an ideal situation for a leachate test would be a very alkaline or very acidic condition. The former is easier to follow by just using water as a leaching medium.

Short-Term Leaching Test

In the development of this testing procedure, a compromise between time and costs of analytical tests had to be reached. The goal was to be able to establish a practical leaching test which would more or less establish the trend of leaching in the field.

The leachate columns were fabricated from four-inch Pyrex tubes having sixty degrees glass funnels fused to the lower end. Glass stopcocks were installed at the stem of each funnel with end tubings leading to 500 ml collection bottles. Leachate samples were collected once a week for a period of one and a half months at room temperature. The volume removed each week was replaced by adding distilled water from the top. Prior to collecting of the leachate, all containers were acid washed with a solution of 1:5 molar ratio of nitric acid to deionized water. Final rinsing with deionized water followed.

The weight ratio of leachant to sample was maintained at 6. Investigators have generally determined that higher ratio of leachant to waste can reduce the possibility of generating common ions and total ionic strength effect which interfere in the solubility of certain compounds.[74] However, using a very high ratio may actually cause dilution of the concentrations of the leached metals. Therefore, a weight ratio of 6 appears to be justified.

Granules produced from 1:2 ratio of sludge to fly ash-kiln dust mixture were prepared following the gradation specified in Table 8. In addition, plain fly ash agglomerated with 16% moisture content was also evaluated.

Comparison of Agglomerates to DOT Standard Aggregates

If the agglomerates are to be used as aggregates, their physical properties have to meet DOT standards. However, due to the small amount of agglomerates available and the large size requirements of the standard tests, Bowser aggregates that have been tested and classified by DOT were therefore used for comparison. Laboratory tests were performed on these aggregates according to the gradations outlined on Table 7.

Bowser aggregates are classified as Class 3 and are of dolomitic origin. Class 3 durability aggregates are those which are associated with little or no deterioration of pavements more than 20 years of age.[74] These samples were selected for their high absorption value in the absence of available lightweight aggregates for testings. From results of standard tests conducted by the DOT, the properties of the aggregates are as follows: specific gravity of 2.44, absorption value of 7-7.6%, 1% freeze-thaw loss using water-alcohol solution as liquid medium, and abrasion wear of 37%.

Results and Discussion

Effect of kiln dust

The influence of kiln dust on the strength of the granules is clearly demonstrated by the results of the performance tests in Table 8. Results are compared to standard DOT aggregates and to pure fly ash agglomerates. High percentage wear and freeze-thaw loss implies poor quality aggregates. Results should at least be as close as possible to those of Bowser aggregates, if not better. Performance of Bowser aggregates in the laboratory tests provide the basis for interpretation of granule quality.

The abrasion test demonstrates the need for the inclusion of lime in the fly ash agglomeration systems. Using pure fly ash alone amounted to complete disintegration of the granules. However, the optimum proportion of kiln dust is not well defined, judging from the results of 5-20% on three different size distributions. The strength is proportional to granule size with the 3/8" showing less degradation. At this particular size, there is no significant difference observed on the strengths of 5, 10, and 20 % kiln dust-granules. Strength test results of 1/2" and graded samples are in conformity with this observation. The high percentage wear for 10% in the 1/2" and graded samples implies the variability commonly

Table 8: Performance test results of the agglomerated electroplating sludge with different percentage of kiln dust as compared to Bowser aggregates and pure fly ash granules

	% KILN DUST				F. A. granules	BOWSER Aggregate
	0	5	10	20		
% WEAR						
3/4"	100	39	48	42		n = 5
1/2", n=3	93.9	26.4	29.7	29.6	34	7.5
(STD.DEV)	2.4	0.9	5.6	2.8		1.8
GRADED	95.3	40.6	50	36.1		
% F-T LOSS						
GRADED, n=5	19.2	9.77	19.0	23.1	1	0.68
(STD.DEV)	1.7	3.2	3.6	0.17		
SG_B	1.87	1.81	2.45	2.05	1.98	2.37
SG_{SSD}	2.05	1.97	2.71	2.21	2.17	2.45
SG_A	2.28	2.17	3.2	2.39	2.45	2.58
SG	2.56	2.44	2.46	2.35	2.56	
% ABS.	9.64	6.73	10.03	9.2	9.63	5.85
Calc. total Porosity	0.269	0.258	4.065×10^{-3}	0.127	0.226	

found in the agglomeration of different materials. Despite the laborious work of trying to obtain a homogenous granule, this proves to be almost impossible with the limited laboratory facilities. It is in this light that the single granule testing is not expected to give a meaningful reading of granule strength, unless large number of samples were analyzed.

In contrast to the sludge-fly ash granules, the pure fly ash agglomerates prepared at a moisture content of 16% compared very well with those containing kiln dust. This is mainly due to the higher percentage of cementitious constituents present in the granules Moreover, it appears that non-homogeneity of the sludge particles created weak spots due to sample discontinuity.

The direct relationship between kiln dust concentration and strength is more evident from the pressure-density compaction analysis shown in Figure 33. Increase in strength is achieved by increasing kiln dust concentration. However, granules of 10 and 20% kiln dust did not exhibit a marked difference in strength. Interestingly, these granules outrank those with 30% kiln dust in trial 9, in terms of strength. Both had similar sludge proportions and total water content at the end of the preconditioning stage. Assuming the difference in soil and sludge properties can be neglected, the 30% kiln dust represents the upper boundary limit in search of the optimum kiln dust proportion. In excess of this, the action of kiln dust can be destructive to the overall quality of the granules.

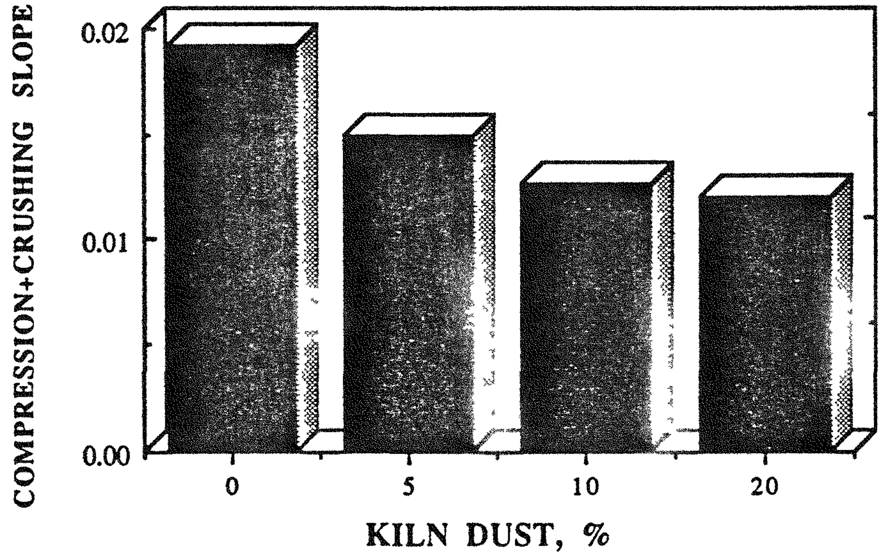


Figure 33. Pressure-density compaction of agglomerated electroplating sludge as a function of kiln dust concentration

The pattern observed in the frost resistance of the agglomerates is the reverse of granule strength. With the exception of that of 5% kiln dust, the change in freeze-thaw (F-T) loss is essentially constant. Granules prepared from 5% kiln dust demonstrate the highest weathering resistance with approximately 10% ± 3% percentage loss.

Table 8 also gives an overall view of the specific gravities and absorption values of the samples. With the exception of 10 and 20% kiln dust samples, the rest exhibit a specific gravity pattern of $SG_B < SG_{SSD} < SG_A < SG$. Among all the agglomerates, the 5% kiln dust had the lowest bulk, SSD, and apparent density, while 10% kiln dust had the highest. A slight fluctuation in the true specific gravities of the samples is observed. Correlating the different specific gravities of the sample suggests that 10% kiln dust is the least porous material. A more direct approach in calculating the porosity of the sample is through the use of Equation 1, discussed in the porosity section of chapter 2. With the bulk and true specific gravities of the sample known, an estimate on the porosity of the sample can be calculated. The table includes the calculated total porosity and confirms our observation that 10% kiln dust is the least porous, followed by 20% kiln dust granules. The total porosity of the granules prepared from 0 and 5% kiln dust is essentially similar to that of plain fly ash agglomerates.

The absorption capacity is almost constant for all samples except for 5 % kiln dust granules. The disparity in the total porosity and absorption values of the granules prepared from 10% kiln dust is worth mentioning. These granules have high absorption but very low porosity. Normally, high absorption depends primarily on the abundance and continuity of the pores. It is obvious that other factors are affecting the properties of the granules. A possible explanation may be attributed to the highly reactive nature of fly ash and kiln dust when exposed to water. Complete hydration may have not been achieved during the agglomeration process thereby absorbing more water. As will be seen in the next chapter, the x-ray diffractogram of this mixture shows lime and tricalcium aluminate which are known to be the reactive components of fly ash and kiln dust. Therefore, despite their less porous structure, their absorption capacity compares with that of a more porous sample. Another possible explanation may be attributed to the capillary action of smaller sized pores. The smaller the pores are, the greater is the capillary attraction for water. The abundance of these fine crevices and the continuity of the pores affect greater absorption of water.

The porosity and absorption of the granules affect their resistance to abrasion and frost damage. Granules with increasing kiln dust concentration exhibit poor freeze-thaw performance due to their less porous structure. As noted earlier, granules made from 5% kiln dust have relatively porous structure but the least absorbent, which explains their higher frost resistance. On the other hand, the granules made from 0% kiln dust manifest the characteristic behavior of aggregates with high absorption and a relatively higher total porosity but failing due to intermittent freezing and thawing. Critical saturation is evidently reached, causing stresses in the granules and eventually leading to disintegration. In contrast, the plain fly ash agglomerates displayed excellent frost resistance, despite their almost similar total porosity and absorption values with that of 0% kiln dust. In fact, their freeze-thaw resistance compares very well with that of Bowser aggregates. A possible explanation may be provided by the mercury porosimetry results in relating total pore volume and pore size distribution.

The comparative study on the agglomerates with either 5 or 10% kiln dust in the inner kernel but with a pure fly ash layering reinforces the benefeciating effect of kiln dust. Table 9 summarizes the results of the performance tests. Comparison of these results with those of 0% kiln dust granules in Table 8 shows a remarkable improvement in the abrasion resistance of the samples. It also emphasizes the importance of strong inner kernel for a more durable composite granule. However, as proven in earlier experiments, kiln dust has the negative effect on freeze-thaw durability tests. This statement appears to hold true only for those granules with certain proportion of kiln dust in their outer layers. Increasing kiln dust concentration in the inner kernel but maintaining pure fly ash layerings actually gives a reduction in percentage of freeze-thaw loss. This result may be attributed to a stronger inner matrix coupled with an increase in the pore volume of the granule layers.

Specific gravities of the samples indicate densification of the solid sample as kiln dust proportion is increased. The calculated total porosity indicates that kiln dust addition on the outer layers of the granules cause a small reduction in total pore volume.

Table 9: Effect of kiln dust on the outer layering of the granules

	1:2 Sl:F.A.+5%K.D.		1:2 Sl:F.A.+10%K.D.	
	F.A.	K.D.	F.A.	K.D.
% WEAR 1/2"	39.00	29.97	37.00	29.70
% LOSS 1/2"	43.11	42.68	34.75	81.559
SG_B	1.48	1.51	1.80	1.86
SG_{SSD}	1.67	1.68	2.00	2.07
SG_A	1.83	1.81	2.24	2.33
SG	2.37	2.44	2.45	2.46
% ABS.	11.00	10.93	10.79	10.29
Calc. total Porosity	0.375	0.387	0.265	0.244

Effect of Curing

Table 10 summarizes the results of laboratory testings conducted on granules with equal proportion of sludge and fly ash-kiln dust mixture. It illustrates the significance of the method of curing on the durability of the granules. The abrasion results show a reduction in

Table 10: Results of laboratory testings showing the effect of curing

	1:1 SL.:F.A.		1:1 SL.:F.A.+20%K.D.	
	A.C.	H.C.	A.C.	H.C.
% WEAR 1/2"	89.83	87.79	29.60	10.55
% F-T LOSS 1/2"	26.711	79.12	64.24	85.45
SG_B	1.33	1.69	1.03	1.44
SG_{SSD}	1.48	1.897	1.60	1.59
SG_A	1.57	2.13	2.39	1.69
SG	2.41	2.42	2.48	2.47
% ABS.	11.51	12.17	19.41	10.55
Calc. total Porosity	0.448	0.301	0.585	0.412

the percentage wear particularly for granules with 20% kiln dust. For pure fly ash-sludge systems, the effect was not very pronounced. These results strongly favor humidity-curing over air-curing for development of higher strengths. Moreover, the effect of kiln dust is once again proven.

In contrast, air-curing fairs better than humidity-curing in terms of freeze-thaw resistance. Over 50% reduction in percentage loss is achieved by the granules containing equal amounts of sludge and fly ash, dropping from 79% for humidity-curing to 30% for air-curing. The results are also very consistent with earlier findings that higher kiln dust content actually cause poor performance during freezing.

Specific gravity and absorption values correlate well with the frost resistance results. The humid-cured granules of 20% kiln dust content have the least total porosity but high absorption, thereby failing very badly during freezing. Of importance is the effect of curing on the absorptive potential of the granules. During air-curing, evaporation of water from the surface occurs. Therefore, hydration reactions are discontinued and the process is not completed. Hydration of the different components required for development of strength and durability takes a considerable length of time. If it is cut short, the pore volume of the sample is considerably larger and explains the large absorptive capacity.

It can be inferred from the experiments that proper curing is absolutely essential in the development of good durability granules. Ambient humidity in the curing area must be maintained at all times if the granules are to cure properly. Normal curing conditions is around 95% relative humidity to prevent the damaging effect.

Mercury Porosimetry Analysis

The total volume of mercury penetrating the solid sample measures the interparticle and intraparticle pores in the granule. A plot of cumulative intruded volume versus radius is presented in Figure 34. Each point on a curve represents a moving average of 9 measurements.

Extrusion curves showing the cumulative pore volume as a function of radius indicate the pore body size of the samples. However, it is recognized that substantial amount of mercury is trapped inside, halting further extrusion. Reasons as to this phenomenon are still being debated and remain unresolved. Therefore, a realistic pore body size distribution from extrusion data is impossible to achieve. Recognizing this limitation, only intrusion curves were analyzed.

There is good agreement between the analysis on specific gravities and absorption with the mercury intrusion porosimetry results. Granules prepared from 5% kiln dust have the highest total intruded volume of 0.1887 cc/gram. Those with 10% kiln dust have the least intruded pore volume, followed by 20% kiln dust. Pure fly ash agglomerates prepared with

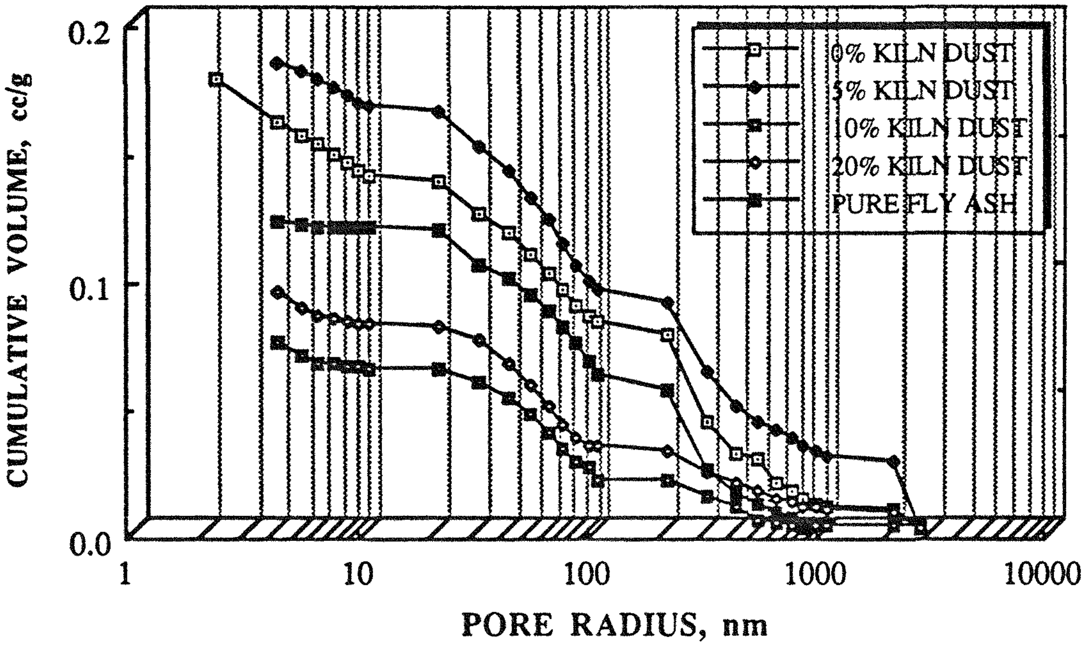


Figure 34. Cumulative intruded volume of the agglomerates as a function of pore radius

16% moisture content have a total intruded volume of 0.1278 cc/gram compared to 0.1683 cc/gram of 0% kiln dust. The latter happens to have the second highest cumulative pore volume. This may be attributed to the presence of sludge particles which cause discontinuity in the matrix compounded by the absence of kiln dust. Evidence has proven that kiln dust results in the reduction of the porosity of the granules. With the exception of 5% kiln dust granules, a reduction in porosity is obtained with increasing kiln dust concentration.

The pore size distribution curves of the granules are presented in Figure 35. The pore volume per unit interval of pore radius is otherwise known as the distribution curve. A summary of the pertinent information is also given in Table 11. The range of pore sizes includes mainly the capillary pores, since gel pores cannot be reached by mercury intrusion.

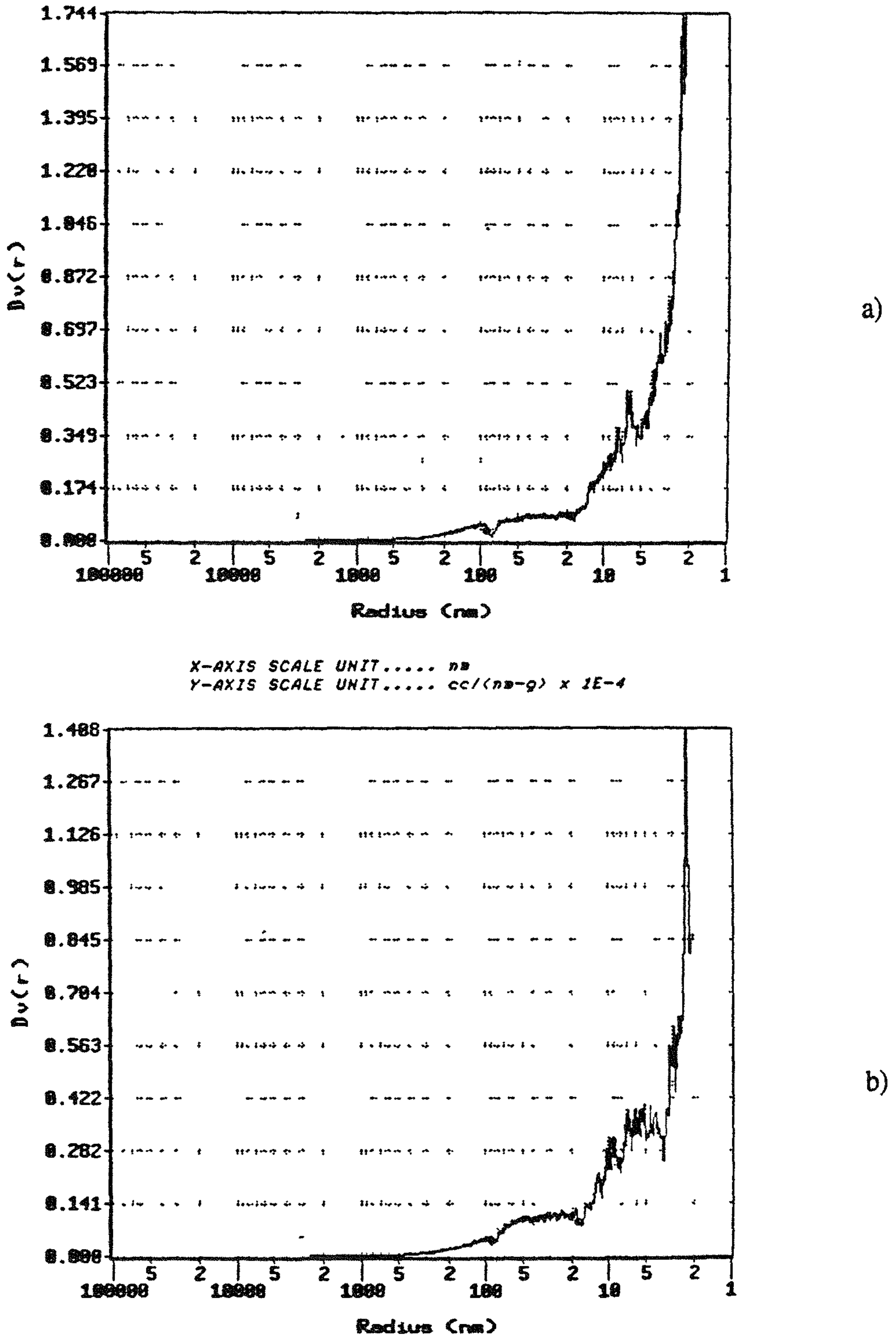


Figure 35. Pore size distribution curves a) 0% kiln dust with 1:2 sludge: fly ash granule, b) 1:2 sludge: fly ash+5% kiln dust granule

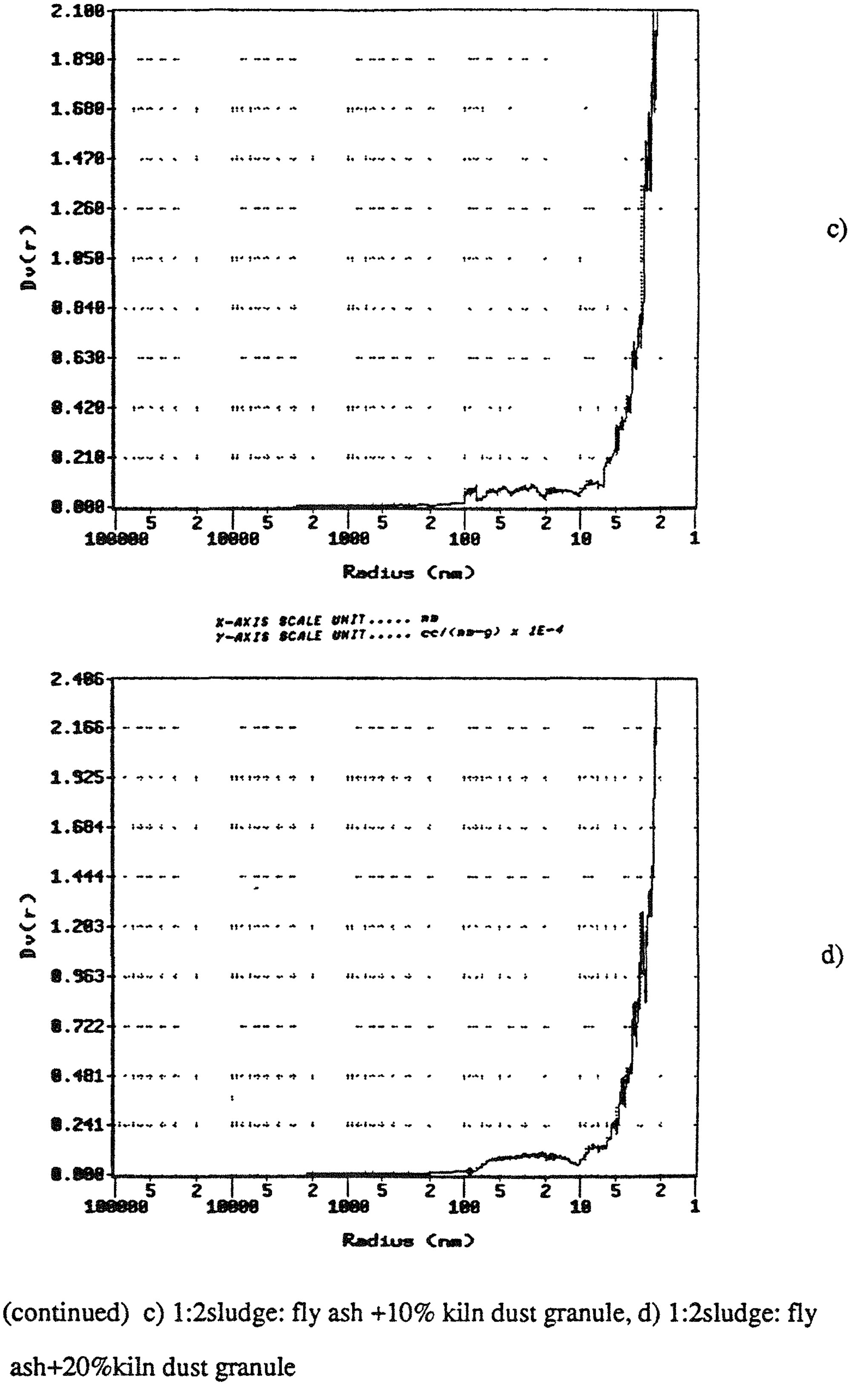


Figure 35. (continued) c) 1:2sludge: fly ash +10% kiln dust granule, d) 1:2sludge: fly ash+20%kiln dust granule

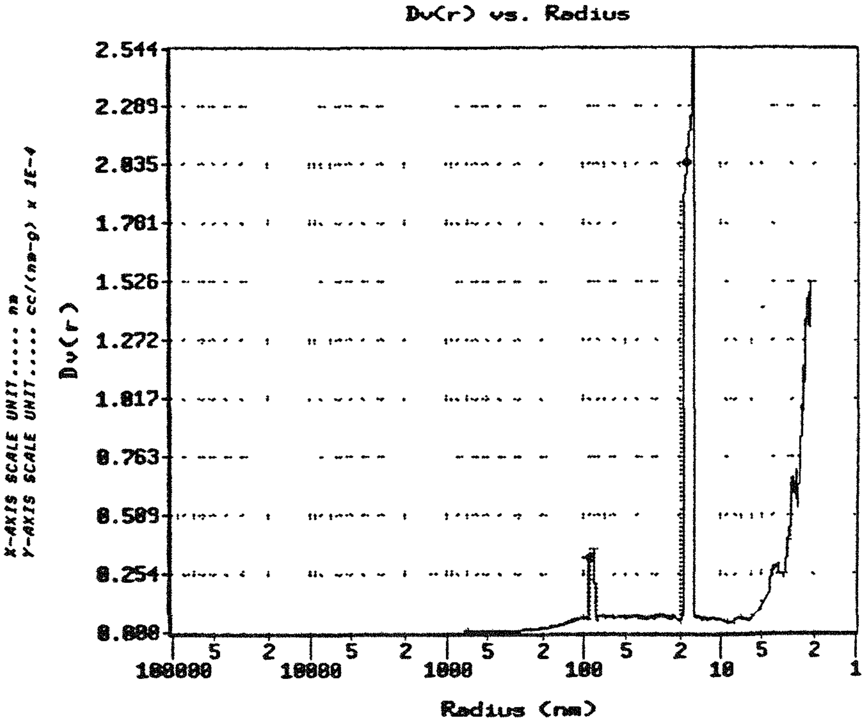


Figure 35. (continued) e) plain fly ash agglomerate

Table 11. Results of the mercury porosimetry measurements for 1:2 sludge:fly ash+kiln dust and plain fly ash agglomerates

	Volume			Pore Number Fraction		
	Mean, cc/g	Mode, cc/(nm-g)	Median, cc/g	Mean	Mode	Median
0% Kiln Dust	0.126	0.000174	0.0841	0.000208	0.0325	0.501
5% Kiln Dust	0.149	0.000141	0.0946	0.000375	0.029	0.504
10 % Kiln Dust	0.0625	0.00021	0.0427	0.000848	0.0288	0.0501
20% Kiln Dust	0.0792	0.000241	0.052	0.00035	0.0387	0.507
Plain F.A. Granules	0.0143	0.00025	0.064	0.000125	0.0622	0.507

It is obvious from the curves that both 10% and 20% kiln dusts have relatively low pore volume distribution in the 10-100 nm radius range. High pore volume was concentrated in the narrow range of 2-2.5 nm. Contrary to this, the volume distribution of 5% kiln dust samples are dispersed from 2.5 to 110 nm. The 4 to 11 nm radius interval has a scattered pore volume distribution of approximately 0.4 x 10^{-4} cc/nm-g, relatively higher than those of 10 and 20% kiln dust granules. The plain fly ash agglomerates exhibit high pore volume in the narrow range of 16 to 10 nm. It appears to have a limited pore radii size but higher than the rest of the samples. This may help explain its excellent frost resistance.

The information given in table 11 is basically similar to what have been previously discussed. It summarizes the cumulative pore volume and the pore number fraction in terms of average, median, and mode values. The pore number fraction represents the fractional amount of all the pores found in that particular radii interval. This table is useful for quick reference on the pattern of the pore size distribution of the different samples.

It can be deduced from these experiments that resistance to freeze-thaw is governed by the pore structure of the samples. Higher concentration of larger size pores permit easy entry and egress of water, preventing freezing of water in the void spaces. On freezing, the water tries to find an escape boundary in order to relieve the hydraulic pressure caused by freezing. In the case of the less durable samples, the bulk of ice formation occurs in a narrower pore size range, exerting greater pressure on the sample. Failure is eventually realized once the tensile strength of the sample is exceeded.

Leachate Characteristics

Results of the leachate characteristics using TCLP and the short-term column method are reported in Table 12 and 13, respectively. Overall performance of the agglomerated granules is outstanding, with respect to their ability to immobilize the metal hydroxides.

Table 12. TCLP results of 1:2 sludge:fly ash+kiln dust and plain fly ash agglomerates

	Elec. Sludge (ppb)	1:2 Sludge : F.A. + Kiln Dust				Plain. fly ash Granule	Detection Limit (ppb)
		0% (ppb)	5% (ppb)	10% (ppb)	20% (ppb)		
Ag	<1	<1	<1	<1	<1	<1	1.0
As	<5	<5	<5	<5	<5	<5	5.0
Ba	10000	420	500	440	340	280	10.0
Cd	10	<10	<10	<10	<10	<10	10.0
Cr	300	540	510	490	810	190	10.0
Cu	540	50	50	50	70	30	10.0
Ni	17000	260	200	60	20	20	10.0
Pb	30	30	40	100	<20	80	20.0
Se	<5	7	10	12	21	27	5.0
Zn	430000	10	20	10	20	<10	10.0
Hg	<1	<1	<1	<1	<1	<1	1.0

Table 13. Results of short-term leaching tests a) third week leachate concentration of granules

Units in ppb	1:2 Sludge : F.A. + Kiln Dust				Pure F.A. granule
	0%	5%	10%	20%	
Ag	<1	<1	<1	<1	<1
As	<5	<5	<5	<5	<5
Ba	160	130	170	130	210
Cd	10	<10	10	<10	<10
Cr	880	710	670	2000	220
Cu	280	280	170	440	10
Ni	10	20	<10	<10	30
Pb	20	50	30	20	20
Se	69	84	47	93	100
Zn	10	40	<10	30	90
Hg	1	1	1	<1	<1

b) fifth week leachate concentration

Units in ppb	1:2 Sludge : F.A. + Kiln Dust				Pure F.A. granule
	0%	5%	10%	20%	
Ag	<1	<1	<1	<1	<1
As	<5	<5	8	<5	<5
Ba	570	210	120	80	650
Cd	10	<10	<10	<10	<10
Cr	180	260	220	760	10
Cu	70	70	50	150	<10
Ni	10	<10	<10	10	<10
Pb	<20	<20	20	<20	30
Se	12	19	13	32	6
Zn	10	10	10	10	20
Hg	1	<1	<1	1	<1

Leachate concentrations are well below the level of concern and meet the minimum requirement for toxic waste stabilization.

Comparison of leachate concentrations stresses the importance of the medium used with respect to the solubility of the metals. Higher concentration of metals which exhibit amphoterism, is observed from the water leachate. Chrome, in particular, shows significant increase in its leachate concentration collected on the third week. In fact, the 20% kiln dust granules have the highest chrome concentration in its leachate. Amphoteric metals in their hydroxide forms exhibit stability only in a narrow pH range of 7.5 to 10. The solubility rapidly increases as the pH approaches either end of the range. Measurements of pH taken from the samples at different periods and at the time of elution, averages at 12.5-13 on the first week and slowly decreasing to 11.5-12 on the fifth week. The pH of the different granules as a function of time is presented in Figure 36. The highly alkaline nature of the solution caused the dissolution of chromium hydroxide particularly for the first week leachate collection. On the fourth week, substantial decrease was realized.

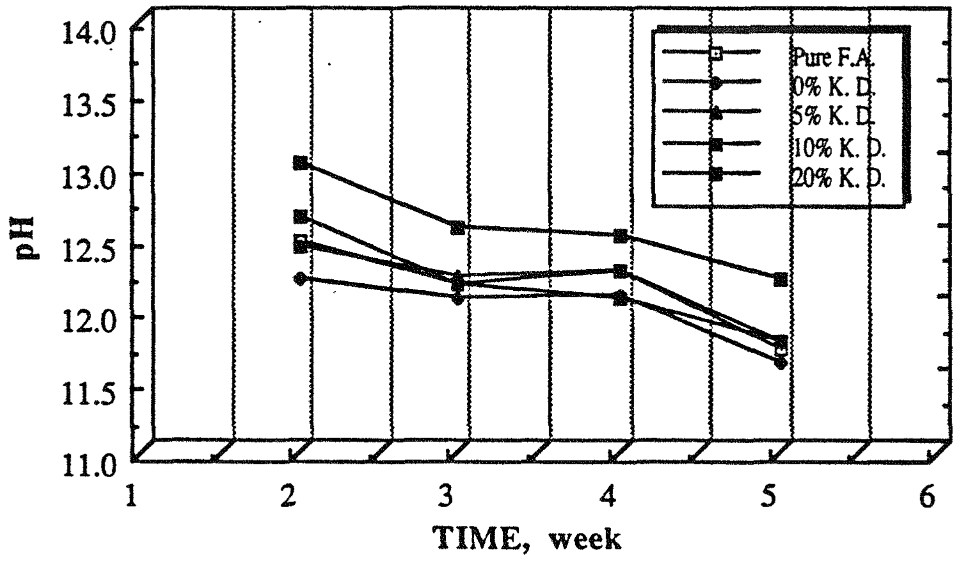


Figure 36. Plot of pH as a function of time for water leachate

The higher concentration of chrome in the water leachate than in the acidic medium may be explained in terms of the stability of the AFt phase. An assumption was previously made and justified by XRD and SEM, that chrome-substituted ettringite does exist in the agglomerates. Bentorite, the chrome substituted ettringite, is stable only above a pH of 11.5-12.[73,75] With the pH of the solution above 11.5, trivalent chrome is contained in the AFt matrix. Leaching of chrome is brought about by the instability of the chromium hydroxide at pH lower than 5 and higher than 10.5.[73] Otherwise, without the bentorite formation, chrome leaching is expected to be even higher than the actual data. On the other hand, the use of acid as a leachant actually neutralizes the alkalinity of the system. This implies the dissolution of bentorite and leaching of chrome. However, precipitation of chromium hydroxide is favored (Ksp of chromium hydroxide is 1.0 x 10-33) which gives the net effect of minimum solubility of the hydroxide compound at pH around 7.5-10. The high "jump" of chrome leaching out from the agglomerates with 20% kiln dust may be explained in terms of the formation of the AFt phase in a saturated lime solution. Discussion will be reserved for a later section.

Concentrations of barium and nickel are higher for slightly acidic medium. Most metals dissolve in an acidic environment with most of the nickel leaching out in the narrow pH range of 5-7.[73] On the other hand, leaching of zinc is initiated at a pH of 5.5-6.2. Studies have demonstrated that leaching of zinc is influenced by the amount of calcium present in the solidified waste.[43] In using high calcium fly ash and lime from kiln dust, the retaining potential of the cementing matrix for zinc is greatly enhanced.

The general trend for the elutions using water as the medium is the decrease in metals concentrations as a function of time. With the exception of barium, reduction in leachate concentration is more effective in the 5% and 10% kiln granules. The concentration appears to increase with 20% kiln dust granules.

Scanning Electron Microscope

The morphology of hydrated phases of sludge, fly ash and 5% kiln dust are shown in Figures 37a and b. An investigation on the structure of 5% kiln dust using two magnifications reveal the encapsulation of particles of electroplating sludge. The rehydration technique applied prior to agglomeration enabled the sludge particles to be ingrained in the matrix. Stronger adhesion between particles is visible through the formation of hydrated phases of fly ash and kiln dust around the sludge particles. Clusters of ettringite and solid spheres of fly ash are well defined. Indentions are visible on the surface due to particles "pop out" during sample preparation. The discernible cracks in Figure 37a were also formed when granules were cracked open for analysis. Notice the void space beneath the particle which appears to be overhanging at the edge. This may represent how macropores are formed during the pan agglomeration process.

The configuration of 10% and 20% kiln dust granules are presented in Figure 38 and 39. The coalescence of smaller granules to the larger ones is illustrated in both photographs. The small spaces surrounding the smaller granules are exposed, and may have been caused by sample preparation. This implies the existence of a maximum size for effective coalescence of smaller granules. Large broken granules tend to be embedded rather loosely compared to smaller ones.

The outer layers formed during agglomeration of the electroplating sludge are visible from Figure 38. It has a homogenous texture from the hydration of fly ash and kiln dust. A closer examination on the hydrated paste of the 20% kiln dust granule shows definite signs of radiating needles deposited on some fly ash spheres. Some fly ash spheres have reacted significantly and are covered with the ettringite needles. Some showed partial deposits of the hydration products while some spheres have not reacted very much. Plowman and Cabrera have suggested that reacted fly ash spheres are generally richer in alumina and poorer in silica

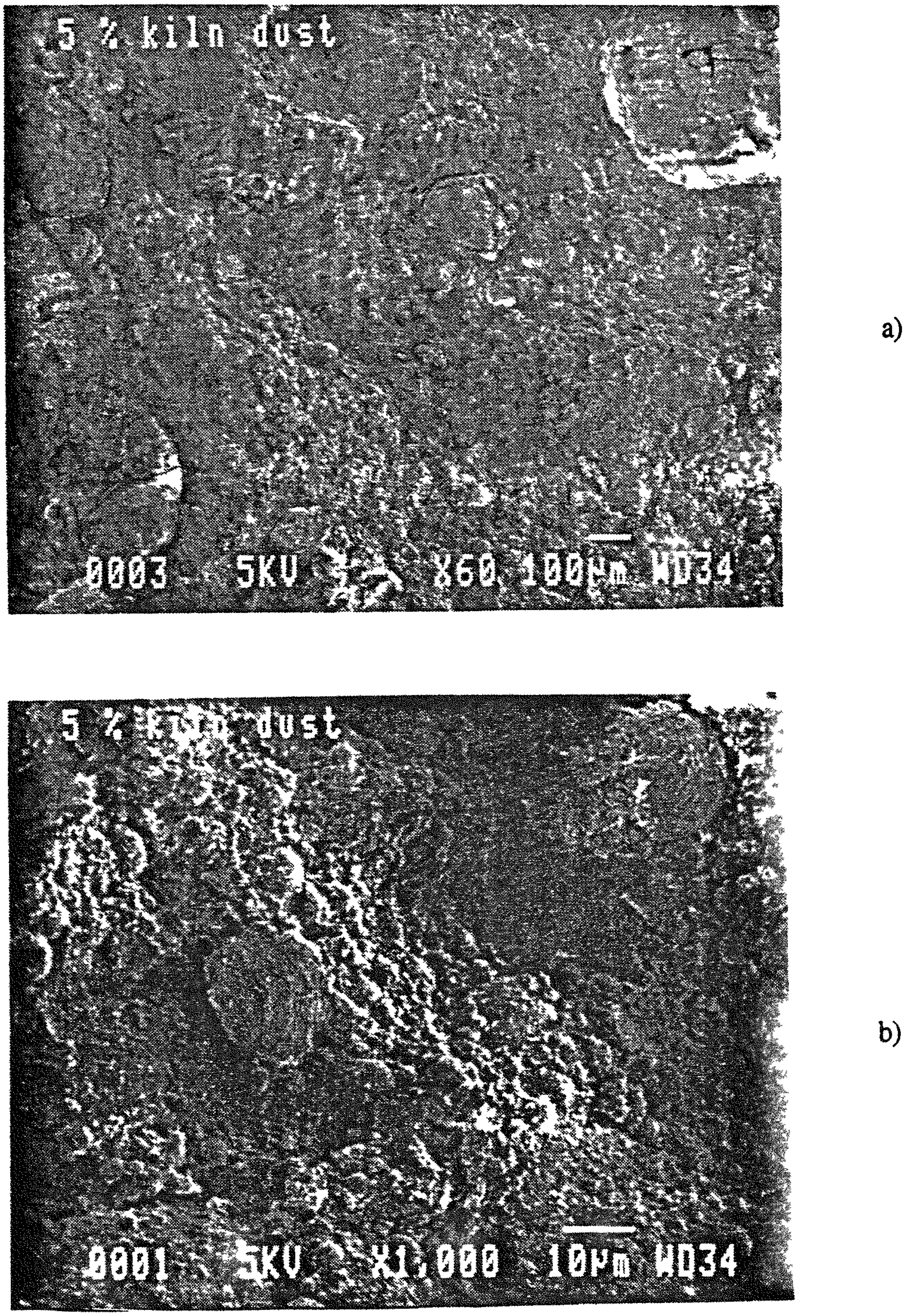


Figure 37. Paste structure of 1:2 sludge:fly ash+5% kiln dust granule a) using low magnification b) using a higher magnification where details in the microstructure and unreacted spherical fly ash particles are clearly evident

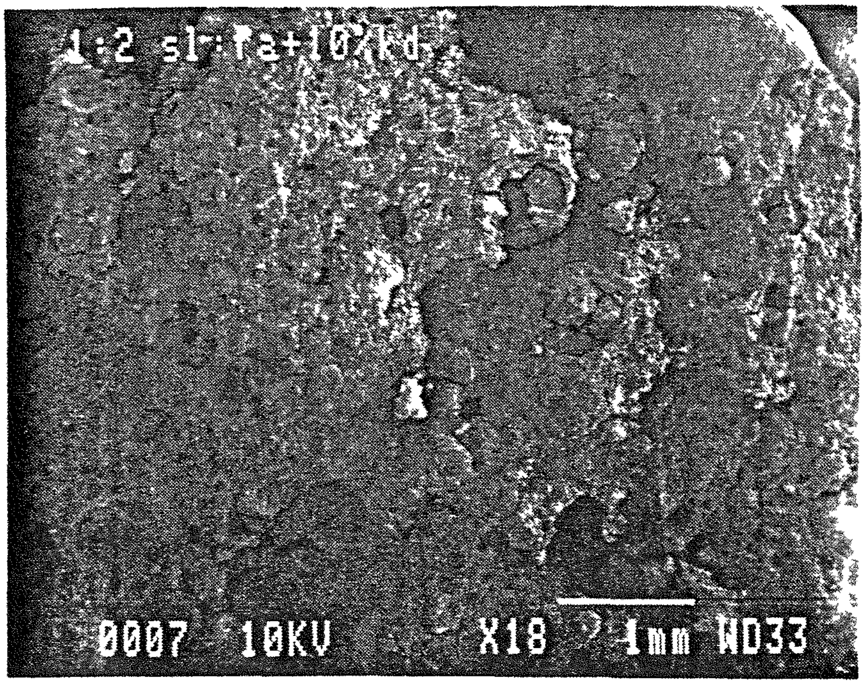


Figure 38. Structure of 10% kiln dust granule showing embedded sludge particles

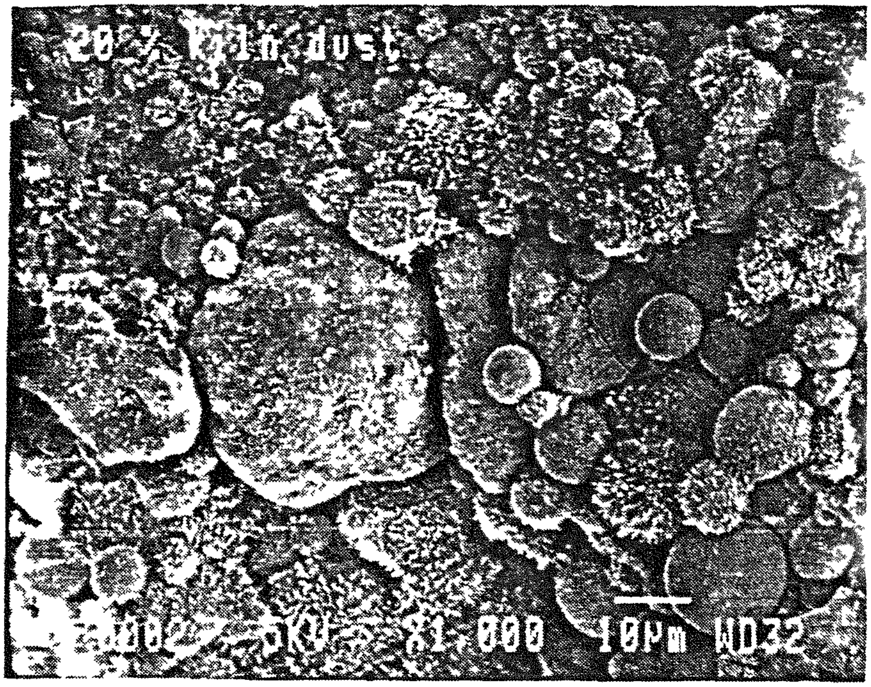


Figure 39. Morphology of the hydrated paste of 20% kiln dust granules

than the unreacted ones.[76] Partial coating indicates that the sphere is partly glassy and crystalline and that the demarcation of crystal products may reveal the glass/crystal interface. Hydration mechanisms of fly ash will be further discussed in a later section. Also evident are the lumps of solidified sludge particles standing out from the center. EDAX analysis shows calcium and silicon as the major elements. Some sludge particles are also entrapped between reacted solid spheres.

Preliminary Evaluation of Agglomerates as Potential Lightweight Aggregates

Results of physical and chemical tests conducted on the agglomerated sludge indicate a potential for use as lightweight aggregate. Leachate results, which are a primary consideration in this metal fixation method, meet regulatory classifications. Of equal importance in the assessment of these samples is their physical durability. Results of laboratory testings will be compared to the performance of Bowser aggregates.

Preliminary testing considered for this purpose consisted of abrasion and freeze-thaw tests. The latter used Method "C" which is for lower quality aggregates. Bowser aggregates exhibited less than 1% loss during 25 cycles of freezing and thawing. From the sludge agglomerates, the highest frost resistance was demonstrated by granules prepared from 1:2 ratio of sludge to fly ash with 20% kiln dust and air-cured. It has an average value of 9.77% ± 3.2%.

Results of Bowser aggregates from 5 trials of laboratory abrasion test gave 7.5% ± 1.8%. The corresponding Los Angeles Abrasion test result has an average of 37% ± 2% which means that the samples will fail anywhere between 4-7 times their laboratory results. Hence, complete disintegration is expected from the granules which were air-cured when subjected to the L. A. abrasion test. The best abrasion resistance is manifested by humidity-cured granules with 1:1 sludge to fly ash ratio and 20% kiln dust. The expected failure of these granules using the abrasion procedure will be anywhere from 42% to 74% percentage wear. This value reflects the abrasion loss for a 1/2" granule.

Based on the quality test limits set forth by Iowa DOT Department, using a gradation number of four in the Aggregate Gradation Table, the maximum loss for freeze-thaw and abrasion are 6% and 50% respectively. The freeze-thaw loss of the 5% kiln dust granules is on the borderline of the maximum allowable, taking the lower end of the range. Unfortunately, its abrasion loss exceeds the specification requirement. Based on these results, these samples may not be used as coarse aggregates for portland cement concrete.

Plain fly ash agglomerates prepared from 16% moisture content show a 34% abrasion wear in the laboratory test. This corresponds to 100% disintegration. Freeze-thaw loss is minimal. Based on these results, these samples would also be rejected for use as concrete aggregates. However, previous studies conducted on using plain fly ash agglomerates as aggregate replacements have proven successful. Concrete specimens containing fly ash aggregates show exceptional strength and are comparable to concretes using natural aggregates.[77] These agglomerates were produced using a commercial scale rotary pan agglomerator very similar to the laboratory disc granulator. The same batch of Lansing fly ash was used for agglomeration in order to minimize variability in chemical compositions. These samples may actually be considered as prototypes of the laboratory scale granules. Hence, the latter is expected to perform as well in concrete as artificial aggregates despite the high abrasion loss. Furthermore, the abrasion test was conducted on 1/2" size granules and do not reflect the performance of the graded samples.

Using the same argument in the preceeding paragraph, the granules containing electroplating sludge may still be used as concrete aggregates. In order for this to be possible, the agglomeration conditions of the sludge agglomerates which performed well in abrasion and freeze-thaw tests shall be integrated. In summary, the best conditions for agglomeration are 5% kiln dust with a 1:2 sludge and fly ash ratio, humidity-cured, and incorporating 5% kiln dust in the outer layerings of the granules. Strength may further be enhanced by reducing the sludge proportion in the granules. Recommendations for agglomeration of possible artificial aggregates are as follows:

1. Preconditioning the sludge prior to agglomeration
2. Using 25% sludge concentration during the preconditioning stage
3. Incorporating 5% kiln dust by weight of fly ash-kiln dust mixture used in the preconditioning and agglomeration stages
4. Humidity-curing of the agglomerated sludge.

Selection of 5% kiln dust granules is a compromise between abrasion and freeze-thaw results. The abrasion resistance is expected to improve by humidity curing of the granules. The lower concentration of kiln dust in the granules may help improve frost resistance. In the course that these agglomerates do not meet standard criteria for portland cement concrete aggregates, the feasibility of using them as granular surface materials or road base/subbase aggregates may be evaluated. According to Iowa DOT specifications for granular surface materials, % freeze-thaw loss should not exceed 20% using Method "C" of the standard tests, and % wear should not exceed 55%. However, additional tests should be undertaken in this aspect.

EFFECT OF METAL-RICH SLUDGE ON THE HYDRATION OF HIGH CALCIUM FLY ASH-KILN DUST SYSTEM

Extensive information is available on the hydration of high calcium fly ash and kiln dust.[33,66,78,79] The major effect in the fly ash-cement systems is the provision of calcium hydroxide which reacts with the calcium aluminate glass to form the calcium aluminate hydrate. In the presence of sulfate ions, alumina in the glass reacts to form the calcium aluminate hydrates, or calcium sulfoaluminates hydrates. The kinetics of reactions are governed by the total concentrations of the different compounds from both fly ash and cement and temperature of hydration reactions. The reaction products of fly ash-cement mixtures are substantially the same as those found in portland cements namely calcium silicate hydrates, calcium aluminate hydrates, ettringite (AFt), monosulfoaluminate hydrate (AFm), calcium hydroxide, and hydrogarnet.[33,78]

Studies on hydration mechanism of the lime-fly ash system are generally consistent with that of cement-fly ash. In summary, calcium ions dissolve in solution and reacts with the silica and alumina to form calcium silicate and calcium aluminate hydrates. The formation of etrringites and mosulfoaluminates is governed by the amount of sulfate ions present. The AFt phase, as ettringite is called, is the stable hydration product if there is an ample supply of calcium sulfate available. If the sulfate ions have been depleted, it readily converts to the AFm phase, commonly referred to as monosulfoaluminate. Ettringite is the major product of hydration observed in this system and has been identified as directly involved in the fixation of the heavy metals.

Lime-Fly Ash System

Takemoto and Uchikawa summarized the mechanism of the paste hydration of fly ash in the presence of lime.[78] The initial reactions commences with calcium hydroxide saturating the solution at a pH above 12.7. At this highly alkaline solution, the SiOH groups on the silica surface are dissociated to SiO^- and H^+ ions. This charge imbalance has to be satisfied to form a stable system and the dissolved Ca^{+2} ions are adsorbed on the negative surfaces. The alkalies in the glass dissolves while thin amorphous Si remains on the surface. $SiO4^{-4}$ and AlO^{+2} in the layer gradually dissolve and combines with Ca^{+2} ions. Solid hydrates are formed increasing the thickness of the layer. Repeated cycles of swelling and destruction by osmotic pressure are experienced by the layer and the reaction continues. Calcium silicate hydrates tend to form on the glass surface while the aluminate hydrates are spotted at some distance from the surface. Alumina ions can diffuse more rapidly than silica and requires higher calcium ions concentration which explains their preferred local sites in the system.

More relevant to the fly ash-lime system is the hydration of tricalcium aluminate (C_3A) in the presence of calcium sulfate.[66] During the dissolution of C_3A in solution, localized concentration of Al-rich amorphous film surrounds the grain. The calcium and sulfate ions in solution adsorb on the surface and the needle-like structures of the AFt phases are formed. It forms an impermeable coating on the reacting C_3A surface, hindering the diffusion of sulfate, calcium, and hydroxide ions. The reaction slows down and an induction period is observed depending on the amount of sulfate ions present. The ettringite coating is disrupted once the hydrating solution becomes deficient in calcium and sulfate ions, transforming into monosulfoaluminate hydrates. The latter is a low sulfate form of ettringite and enters into a solid solution with C_4AH_{13} especially at room temperature.

Formation of ettringite is therefore, sulfate-dependent. The solubility of calcium sulfate is shown to decrease in a lime-saturated solution.[79] The solubility of lime is also reduced slightly by increasing the amount of calcium sulfate in solution. This retards ettringite formation which favorably influences the properties of the paste. Ettringite formation is accompanied by great reduction in the amount of water available in the vicinity of the hydrating compounds where it bounds approximately 26 molecules of water in the formula unit. The expansive nature of ettringite causes a reduction in strength gain of the mixture.

SEM studies on different proportions of fly ash and kiln dust in the hydrated paste show typical hydration products in a lime-rich system, as evident in Figure 39. These samples were prepared in the laboratory using the same Lansing fly ash. Thin prismatic crystals of ettringite are well-dispersed in 5, 10, and 15% kiln dust -agglomerates. Platy crystals of AFt phases and AFm phases such as monosulfoaluminate are also visible in Figure 39a. The large monolith structure labelled as A in Figure 39b has been identified as straetlingite, a calcium-aluminate-silicate hydrate containing some iron impurities. The energy spectrum collected for structure A is given in Figure 40. The solid sphere labeled b in Figure 39c shows massive deposits of radiating needles of ettringite on one side while the front part is barely covered. The demarcation of the surface products identified the aluminate glass interface from that of the silica rich crystalline side.

Fixation method

The hydration characteristics of the fly ash-kiln dust system were evaluated in the presence of metal-rich sludge. Samples of sludge and fly ash were mixed in water, using 25%, 50%, and 75% sludge by weight of mix. One sample was prepared using a 1:1 ratio of sludge to fly ash and about 20% kiln dust. Qualitative analysis of these samples were performed through the use of XRD, SEM, and thermal analysis methods. The latter made used of thermogravimetry (TG) using TGA V5.1A Du Pont 2000. The conditions for running were in an inert atmosphere of N_2 gas, heating rate of 10 degree/minute, and a maximum temperature of 980^{o}C.

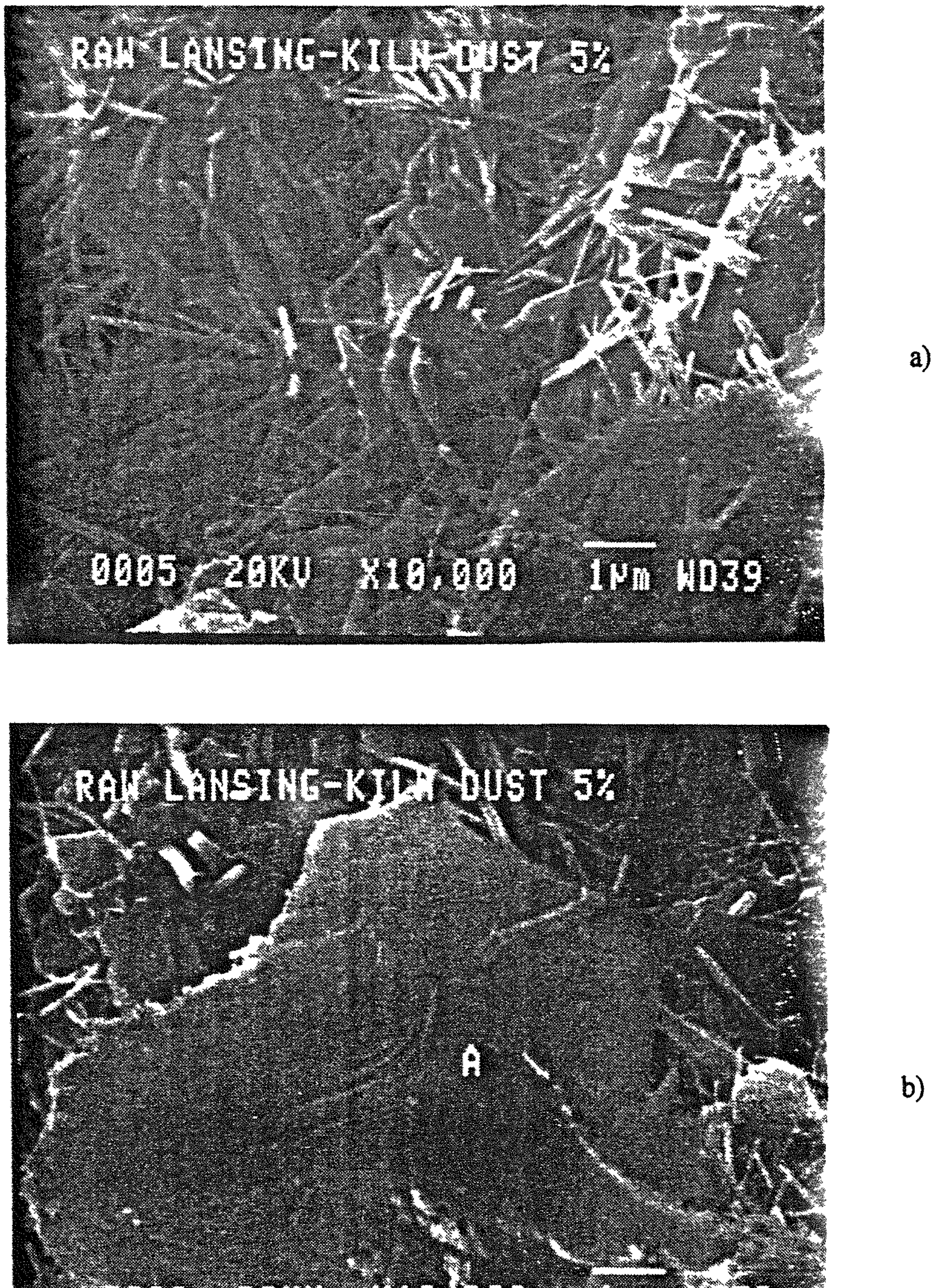


Figure 39. Hydrated paste of high calcium fly ash with different kiln dust concentration a) formation of AFt phases for 5% kiln dust; b) calcium-rich silica hydrate in the 5% kiln dust granules surrounded by ettringite needles and platy crystals

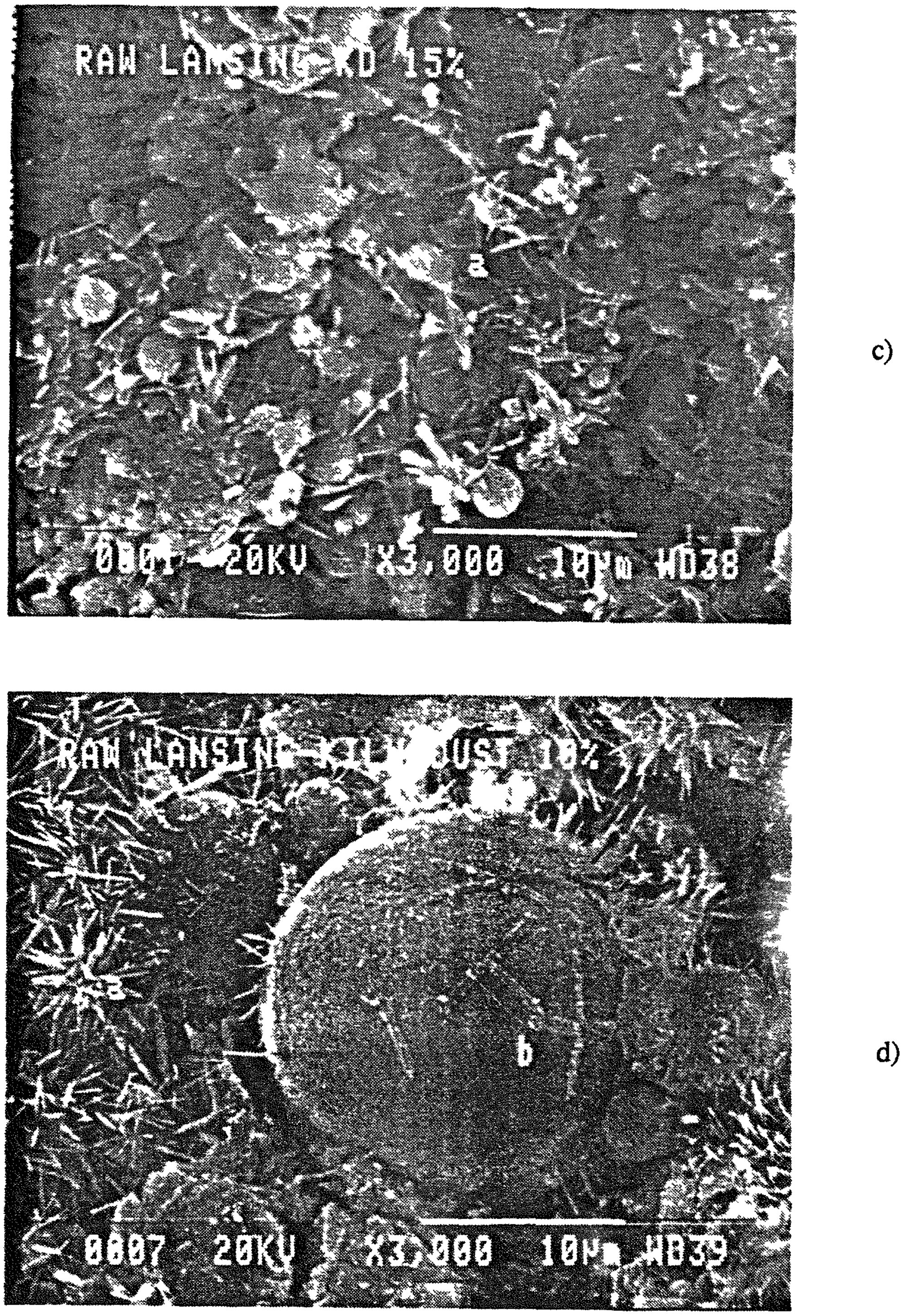


Figure 39. (continued) c) spherical fly ash glass showing demarcation of glass and crystal interface; d) 15% kiln dust-fly ash granules showing growth of massive crystals

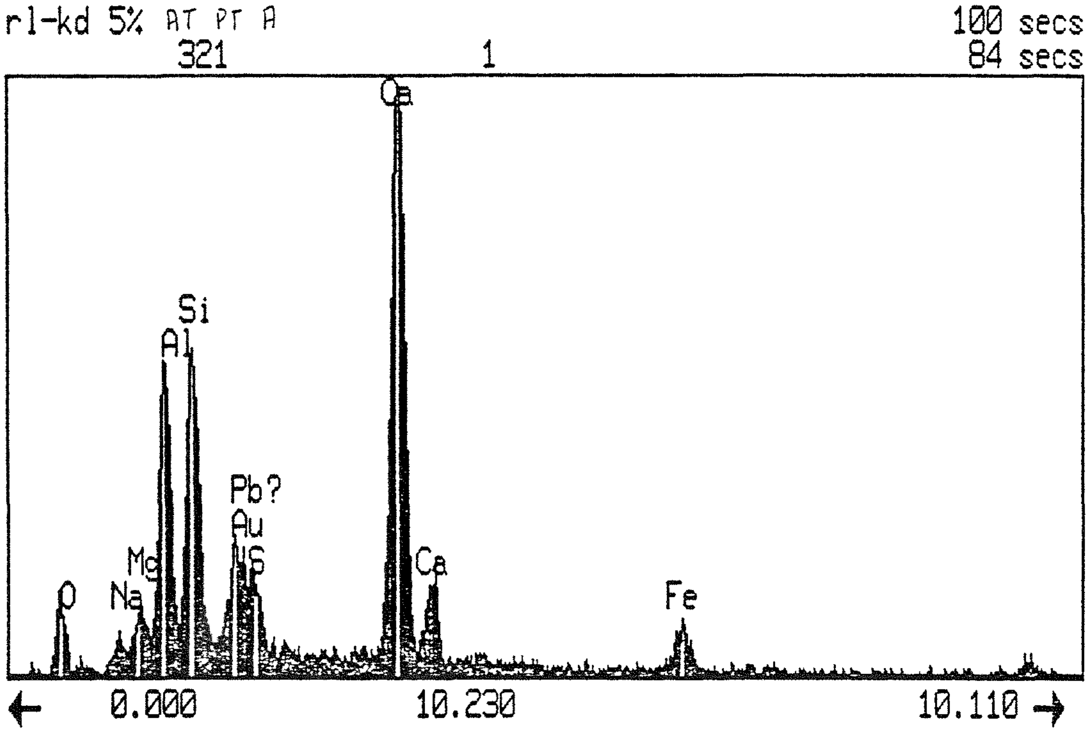


Figure 40. Energy dispersive x-ray analysis of straetlingite present in 5% kiln dust

<u>X-ray diffraction</u> The diffractograms of 25%, 50% sludge and 20% kiln dust in Figure 41 are characteristic of hydrated fly ash-kiln dust systems. Crystalline structures of AFt phase, periclase, quartz, and calcite are the major phases in these proportions. Partial substitution of aluminum by chrome appears very possible as indicated from the pattern of 1:1 sludge to fly ash ratio. This is isostructural with ettringite and is identified as bentorite. Furthermore, some form of sodium zinc sulfate and gehlenite are also observed. Similarly, the sample with 20% kiln dust also appears to have chrome substitution. As the amount of fly ash is increased to 75%, ettringite peaks govern the pattern. Strong lines of lime are also identified.

The incorporation of 75% sludge in the mix gave an abrupt change in the pattern. No traces of ettringite can be located in the pattern. Major phases consist of calcite, quartz, and

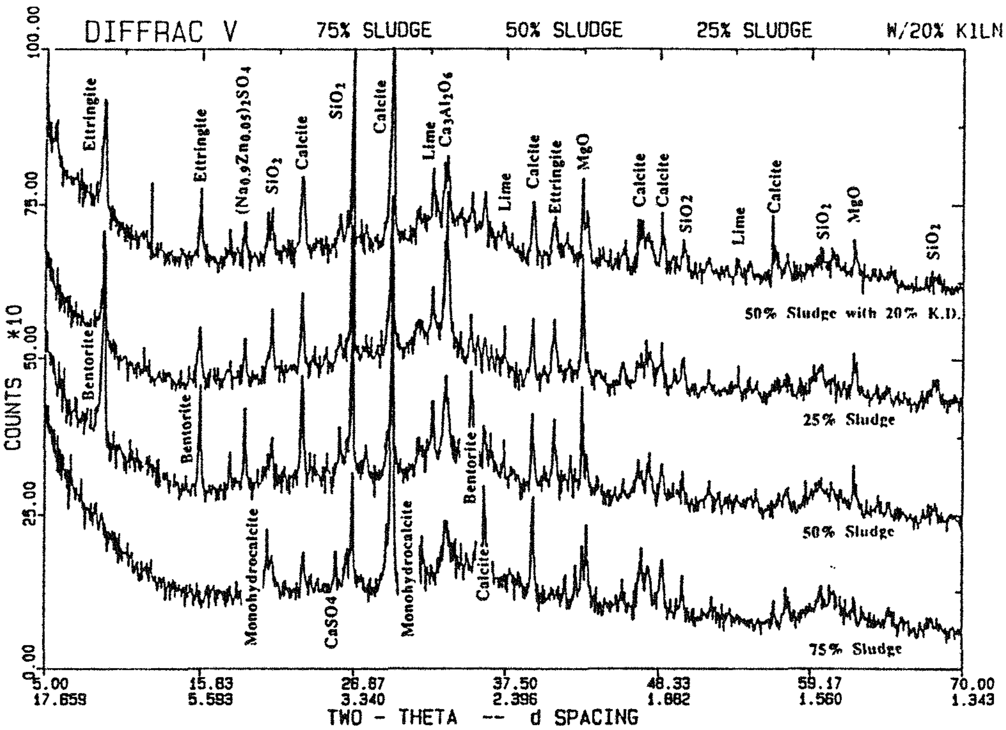


Figure 41. X-ray diffraction pattern of different proportions of sludge and fly ash

periclase. Monohydrocalcite which is essentially a calcium carbonate hydrate, together with anhydrite, zincite (ZnO), and an iron sulfate hydroxide hydrate make up the minor phases in the systems. The disappearance of ettringite from the pattern may be attributed to several reasons. The basic premise of sufficient amounts of calcium, alumina, and sulfate ions in solution may not be met. Despite the availability of both calcium and sulfate ions, alumina ions may not be present in appreciable quantity to effect formation of ettringite. Another most likely possibility is the existence of a low sulfate form, AFm phase with chemical formula of $C_3ACaSO_4 \cdot 15H_20$. It has a characteristic line at 10.3 Å in place of the 9.7 Å basal spacing. It maybe present in an amorphous form which explains why there was no characteristic d-spacings collected in the pattern.

Thermogravimetry Complete thermal decomposition behavior of the sample can be determined using thermogravimetry. A plot of weight, either in mass or in percentage, against temperature (°C) measures the change in weight while the sample is being heated. It is usually employed in conjunction with derivative thermogravimetry (DTG), which is a method of expressing the results of TG by giving the first derivative curve as a function of temperature. DTG, therefore, plots the rate of weight change versus temperature.

Incorporating DTG in the analysis of the data has several advantages[80]. First, overlapping reactions of complicated decomposition processes may be more discernible from the DTG curve. Similarly, the temperature at which the maximum weight change is easily identified. Lastly, the DTG curve resembles differential thermal analysis (DTA) and differential scanning calorimetry (DSC) curves which may assist in the interpretation of the data.

In analyzing the data, the last advantage of using DTG curve, was fully employed. Identification of the patterns was accomplished with the aid of published works on thermal analysis of cement and pozzolanic systems and the knowledge of thermal equilibrium of the compounds identified through XRD.[66,79,80,81]

TG and DTG curves of the samples are presented in Figure 42. In addition to the samples containing different proportions of sludge and fly ash, the electroplating sludge and plain fly ash granule prepared with 16% moisture content were also analyzed. The analysis of the sludge and pure fly ash granules will be discussed first.

Initially, the loss of surface water and other loosely bonded water accounts for the large drop in the weight of the samples. This holds true for all the samples and appears as a tall peak in the DTG curve. For the electroplating sludge, moles of water from goethite lost at 136°C were also covered by this peak. The second peak indicates the loss of 2 moles of water of chromate at around 200°C. A small but wide peak commencing at 210°C and ending around

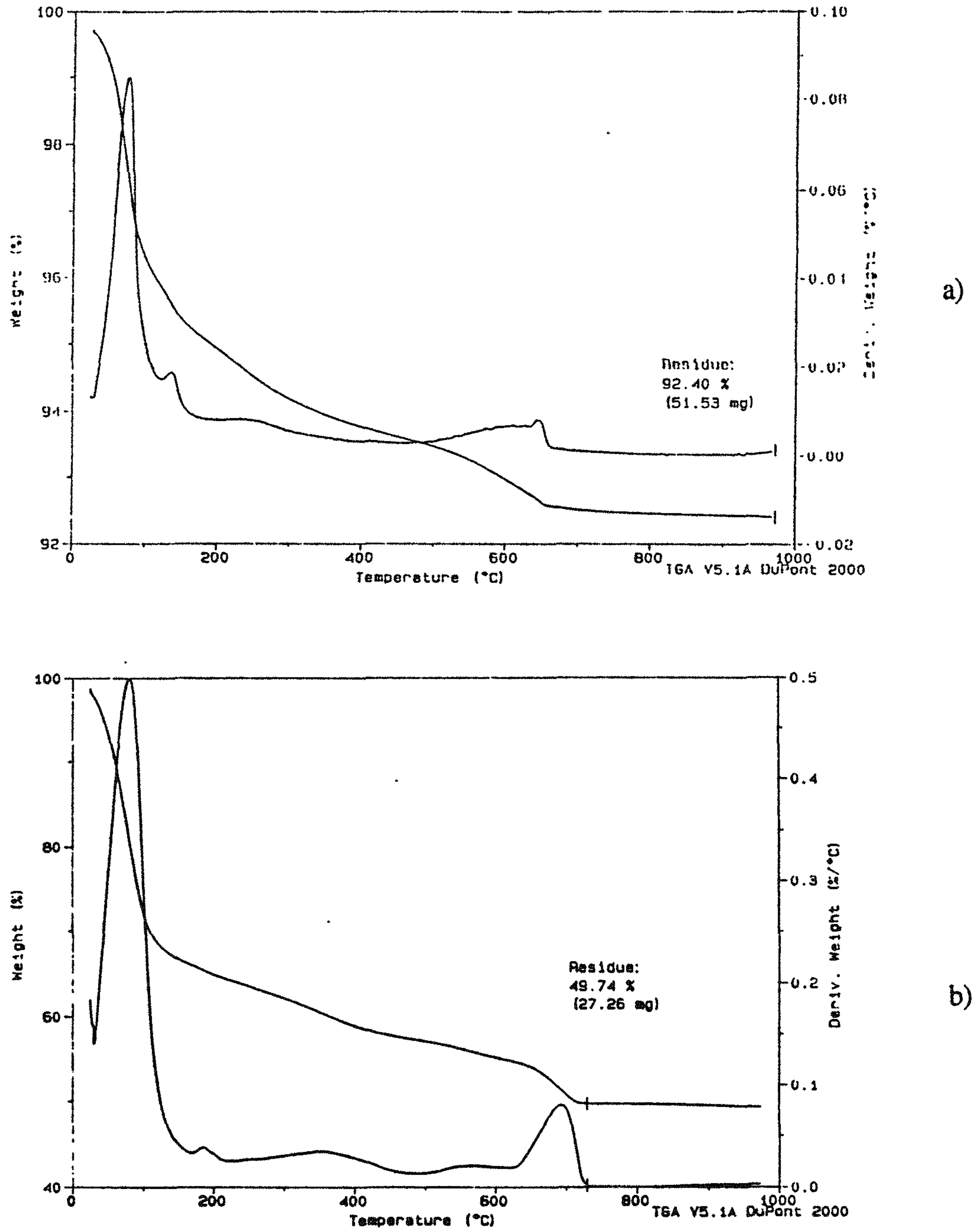
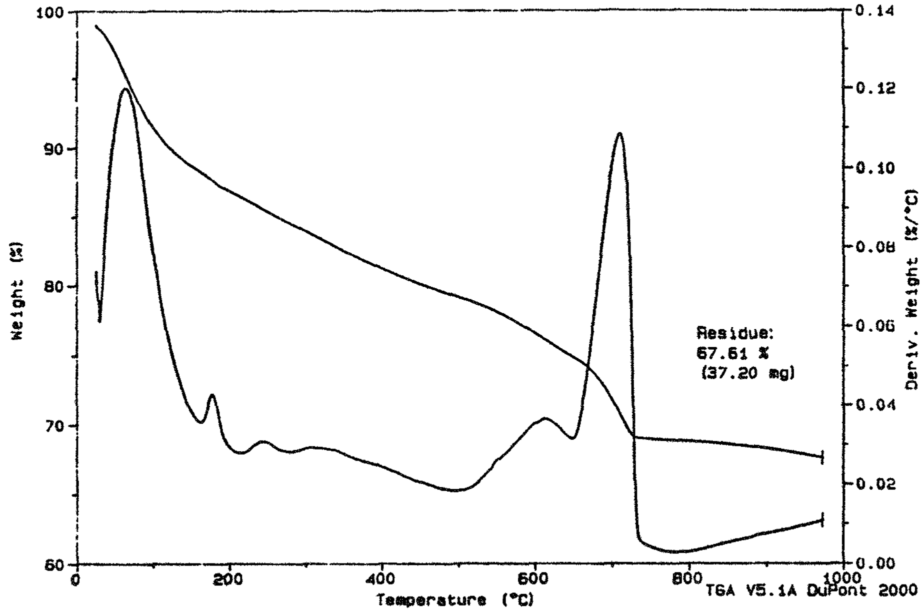
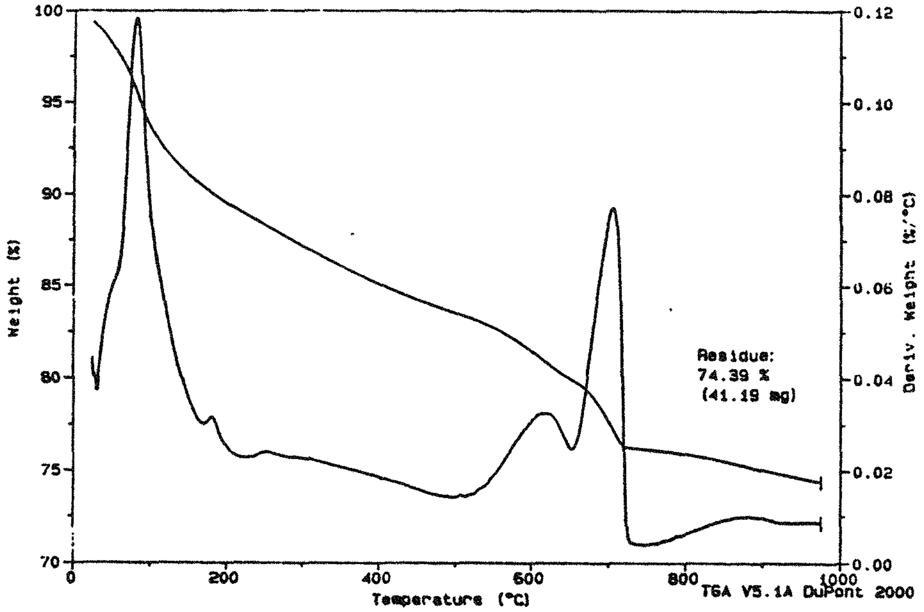


Figure 42. TGA and DTG curves a) agglomerated fly ash with 16% moisture content, b) electroplating sludge



c)



d)

Figure 42. (continued) c) 75% electroplating sludge mix, d) 50% electroplating sludge mix

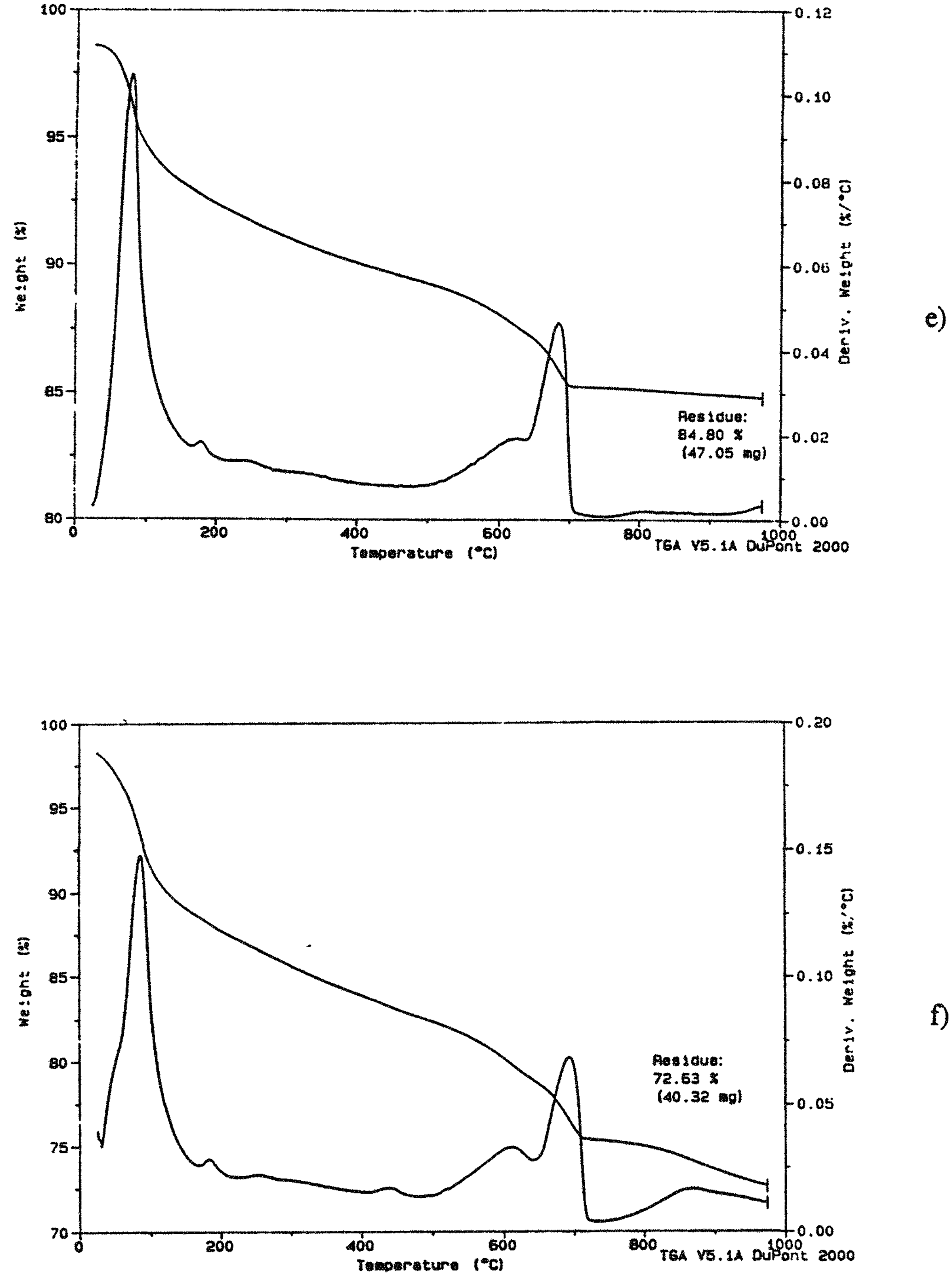


Figure 42. (continued) e) 25% electroplating sludge mix, f) 50% electroplating sludge, 50% fly ash+20% kiln dust mix

440°C indicates further dehydration of $Fe_2O_3 \cdot xH_2O$. Transition from α-quartz to its β-form occurs around the 573°C. Finally, the last peak is the decarbonation reaction of calcite at 500-600°C, yielding lime and carbon dioxide. Normally, decarbonation of calcite happens around 900°C. However, if calcite is mixed with quartz and other decomposition products that react with lime, the reaction becomes significant at this temperature.[66]

For the agglomerated fly ash, successive dehydration of ettringite was evident. Around 160°C, 48 interstitial moles of water were lost, followed by decomposition of hydroxyls bound to aluminum ions. Dehydration leaves at least one or two moles of water of ettringite, even at very high temperature. Ettringite decomposition at higher temperature yields the monosulfoaluminate form.

The TG and DTG curves of the rest of the samples follow the same decomposition routes as described above. The only difference which can be observed from the curve is the occurrence of another peak around the 800-900°C range. This indicates the existence of ettringite (AFt) phase and a carbonate-substituted AFm phase. The last compound is a low form of calcium referred to as carboaluminates and dehydrating at 230°C and around 900°C. Decomposition at this temperature arises mainly from the liberation of carbon dioxide gas.

The results from this test strongly supports the existence of an AFm phase, with both sulfate- or carbonate-substitution, in the 75% sludge mix. In fact, to verify these results, SEM photomicrograph of this mix proportion was taken and is presented in Figure 43. Clusters of calcite particles are evident. No needle-like structures can be observed at this high magnification. However, some hexagonal plates of the AFm phase may be present using an even higher magnification. Solid spheres of fly ash are also present.

General summary

The effect of heavy metal hydroxides in the hydration of fly ash and kiln dust is negligible. The mechanism of formation of both the AFt and AFm phases proceeds in the

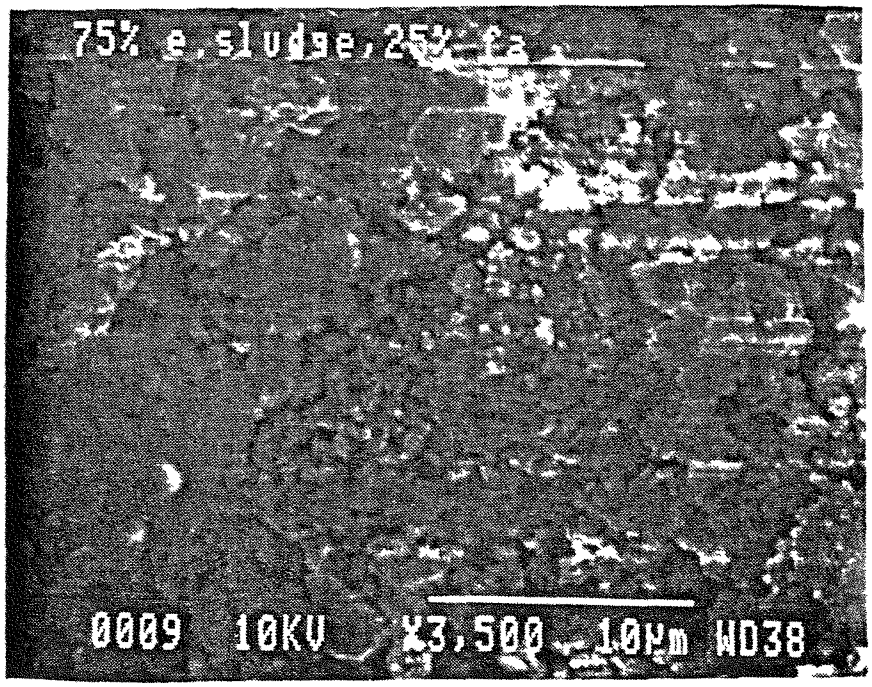


Figure 43. Absence of AFt phases in the 75% electroplating sludge-fly ash mix

usual fashion. In fact, the chromium substituted hypothesis is being investigated at North Dakota universities and the results have proven to be successful.[70,75] Substitution is provided by the hexagonal structure of ettringite which is columnar in nature. Sulfate ions and additional water molecules are located in the channels of the columns and other ions can completely or partially replace sulfate. Al^{+3} may also be partially substituted by Fe^{+3} and Si^{+4} or even chromium, in this particular case. The highly alkaline nature of the fly ash and kiln dust is generally sufficient for ettringite to remain fully stable.

The importance of ettringite formation in a lime-saturated solution can not be overemphasized. In explaining the high chrome concentration in the elution of 20% kiln dust using water leachant, kiln dust plays a critical role. The high lime content in solution retards ettringite formation and thereby, lessens chances of substitution. Therefore, chrome exists as hydroxide which exhibits increasing solubility beyond a pH of 10. This leaves a high concentration of chrome in solution which is evident from the leachate results.

The rate of paste setting is influenced by the amount of kiln dust in the system. Since the growth of the needle-like structure of ettringite is retarded in a saturated lime solution, larger sizes of hydrated crystals are formed.[66] The forms of these hydrates depends on the relative concentration of calcium, aluminate, and sulfate ions in solution. Increased volume of the hydration products leads to a decrease in the distance between particles. The immediate effect is quick set. In contrast, the fine nature of the ettringite crystals maintains plasticity of the system. Transformation of the fine-grained ettringite into large needle-like structures bridges the spaces between particles, producing a rigid structure. Normal setting is observed. In the absence of gypsum, large tabular crystals of calcium aluminate hydrates are formed which cause rapid setting. This behavior was observed in the preconditioning of the sludge in both phases. It gives a better explanation of the relatively low amount of kiln dust compared to fly ash used in the preconditioning stage. It also covers the lower optimum moisture content of the granules upon addition of kiln dust.

CONCLUSIONS AND RECOMMENDATIONS

The major conclusions derived from this study are:

1. The fly ash-based solidification/stabilization of heavy metal hydroxide sludge is a promising waste management technique. It utilizes the cementitious properties of Class C fly ash, treating the waste as a resource. It provides a safe co-disposal of fly ash, electroplating sludge, and kiln dust.
2. Application of the agglomeration principles as means of fixation method proved successful. First, it provides durable coating on the toxic particles thereby increasing their degree of protection from the environment. Secondly, the surface area of both the sludge and fly ash particles is greatly reduced, minimizing leaching potential of the toxic components.
3. Encapsulation by agglomeration is a simple and inexpensive method of waste treatment and disposal.
4. Metal salts can be stabilized by the addition of high calcium fly ash through metal hydroxide precipitation dispersed in a cementitious matrix. Both chemical and physical encapsulation are the operative mechanisms of fixation. However, the degree of immobilization is strongly affected by the chemical stability of the treated waste in a highly alkaline environment.
5. The optimum moisture content of the granules is a function of the physical and chemical composition of the feed material. Single agglomeration of fly ash has its optimum value at 14-16%, while addition of kiln dust places it at 10-12%.
6. Incorporation of kiln dust contributes to the strength development of the granules. However, the frost resistance of the granules decreases with increasing kiln dust

content. A compromise has to be reached to satisfy both strength and frost durability requirements.

7. A stronger matrix of fly ash and kiln dust is possible by controlling the amount of kiln dust in the mix. Formation of ettringite during the hydration is accompanied by large volume increase. With the lime-saturated solution, ettringite growth can be retarded.

8. The pressure-density compaction test is a reliable qualitative procedure in comparing granule strength. Granule size and shape effects are minimized. Additional information may be obtained by sieving the granules using the last mesh sieve size in building up the sample. The weight loss may then be calculated as a percentage of the original weight.

9. Preconditioning of the sludge prior to agglomeration increases the strength of the granules and also eliminates the need for double agglomeration.

10. Fixation of potentially hazardous metals through ettringite formation may be possible by increasing the stability of the AFt phase in solution. Excess supply of sulfate ions should be available and pH should be regulated above 12.

above 12.

11. The aggregate potential of the agglomerated sludge may be increased by limiting kiln dust concentration at 5% and subsequent humidity-curing of the agglomerates.

The results of this investigation are in no way complete and should be taken as starting points for further research. Recommendations for further studies include the following:

1. A comprehensive study on metal-substituted AFt phase as means of stabilization. Synthetic ettringite may be produced for laboratory testings and analyzed using the available techniques.

2. Investigation of the fixation mechanism at different stages of hydration in correlation with their respective strengths.
3. Longer leaching period using water and dilute acetic acid as medium by column method. The resulting leachate would be analyzed for trace metals composition. The stability of certain heavy metals is known to vary depending on the alkalinity or acidity of the solution.
4. Agglomeration of the granules based on the recommended procedure and further testing as potential lightweight aggregates. Concrete molds for compressive strength and freeze-thaw tests may be prepared in order to evaluate their performance in concrete. Results may be standardized using available lightweight aggregates as control samples.
5. Pilot scale application of agglomeration as a means of fixing metal-rich sludge. In this way, large volume of agglomerates may be evaluated using ASTM standard testing procedures.
6. Agglomeration by briquetting method and utilization of the solid bricks in construction.
7. Use of the sludge-fly ash-kiln dust system as road base material.
8. Utilization of other coal combustion by-products as stabilizing agents and in improving strength properties of the agglomerates. High volume application of fluidized bed residue and bottom ash are already being initiated. The feasibility of using these waste materials in the field of chemical fixation and solidification of hazardous wastes should be investigated.

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