Executive Summary

A detailed review of the work carried out on the development of concrete is given in the chapter 1. The Comprehensive literature overview and the basic chemistry involved during its formation, role of different type of materials used for the development and their effects on the mechanical, chemical and engineering properties is discussed. Factors affecting mix compositions, such as curing temperature, curing time, admixtures, water/binder ratio, permeability, pH, porosity and water/solid ratio are also discussed in detail. Application and techno-economic analysis of concrete is also discusses.

Chapter 2 explains experimental part of the work. Characterization of the selected material which is to be use is also done. Two types of concrete were prepared during the study (i) Fly ash based, (ii) sludge and fly ash based. Cubes of 10cm x 10cm x 10cm were prepared from the mixture containing different fly ash to cement ratio, and fly ash to sludge for unconfined compressive strength. 5cm x 5cm x 5cm cubes were also prepared and used for further analysis.

Physico-chemical analysis and heavy metals estimation were performed by (APHA, 1998) standard method. Heavy metals like Pb, Fe, Mn, Zn, Cu, Ni and Cr were estimated by atomic absorption spectrophotometer. Durability testing was performed to access the effect of environmental stress and strain condition on the solidified/stabilized products. Performance of developed concrete and its effect on the immobilization of toxic metals were also studied through modeling (Geochemical modeling) and statistical analysis. Microstructural characterization was also performed to study the changes occurring during the reaction.
Chapter 3 is determining the compatibility of sludges with concrete. Experimental work has designed for multi metal bearing sludge, single metal bearing sludge and control by changing the various materials such as cement and sand. The developed concrete is being assessed on the basis of various engineering properties of concrete. In order to simplify the development process, the compressive strength was selected as one of the benchmark parameter in the structural design of concrete structures. Sample preparation was done by selected (M15) mix proportion. The prepared specimens were cured at ambient conditions for 7, 28 and 90 days in triplicates. Unconfined compressive strength testing was performed on developed concrete after curing period.

Results indicate that the strength of 90 days was high for all the ratios as compared to 7 and 28 days of curing. Change in the strength was not found to be very effective for 28 and 90 days of curing. Hence 28 days of curing was sorted as the final curing period for the further experiments to study the effect of the cement, sand replacement with fly ash and sludge respectively. Reference samples were (Hp) attained 9.5, 12.3 and 14.8 MPa strength for 7, 28 and 90 days of curing. Samples containing 75% waste (Single metal bearing sludge) gain 0.5, 0.9 and 1.4 MPa strength after 7, 28 and 90 days of curing. Multi metal bearing sludge was found more feasible to developed concrete through S/S process.

Chapter 4 is based on the utilization of fly ash and hazardous solid waste (sludge) to prepare concrete with long-term fixation and geochemical modeling and statistical interpretation were used for further prediction. This chapter is divided into two parts: In part “A” pH has studied in connection to its effect on the mobility of the elements, as there is a relative tendency that matrix with high compressive strength has fixed
efficiently. Samples were analyzed in extreme chemical environment and observed its effect on the stabilization of metals at different pH & curing days. pH was fixed for each leaching test which affects the conductivity of the sample. Lowest pH shows high conductivity. Significant portion of the heavy metal ions are precipitated in their least soluble forms within high alkaline pH condition (7 – 11). Leaching pattern for anions and cations was similar for 7, 28 and 90 days of curing and fixed at 2 -10 pH. The leaching behaviour of heavy metal is indeed known to be pH dependent. Fixation of metals increased with increase in the pH up to 10, after that solubility increased. 7 and 28 days of curing are sufficient for the fixation of heavy metals present in the waste. It was observed that leaching at 28 days curing was high as compared to 7, 90 days curing for entire W/B (Waste/Binder) ratio. Another finding of these experiments is that, the risk of contamination due to release of heavy metals from concrete on-site appears low. Fe fixation is found minimum rather than other metals due to high content in raw material. Ni, Mn and Pb were found in very least quantity, they were easily fixed in the developed matrix. Cu and Ni metals were completely fixed in pure & cement/fly ash samples like; Cp, Sp, Fp, Lp. Metals show maximum fixation with given curing days; Cu at 7 & 28 days, Cr at 7 & 90 days, Zn at 7 & 90 days, Fe at 28 & 90 days. Results indicate that 70% to 90% of metals (Fe, Zn & Cr) were retained in the concrete matrix. Wherever, Pb, Mn, Cu & Ni metals were completely fixed in the matrix. The fixation of Heavy metals in the pH ranges from 2 to 14 is in order of Pb<Ni<Cr<Cu<Zn<Fe.

It is clear from the SEM micrographs of concrete samples cured for 28 days that the development of microstructure was improved due the pozzolanic contribution, which resulted in the formation of clusters of hydrated products and other compound like CSH,
Portlandite, ettringite, metal complex etc. Ettringite & CSH are important hydration product commonly found in concrete. The micrograph spectra show the presence of large quantities of CSH that would be indicative of a pozzolanic reaction. Due to the formation of hydrogenate phases most of the heavy metal trapped in concrete. Excepting L2 sample, all sample shows high amount of crystalline structure. It is conformed by EDX analysis, that the developed concrete content high amount of silica, calcium, aluminum percentage.

In part “B” pH of the environment was affected by the release of many toxic elements from the matrix. In addition, geochemical speciation modeling also can provide useful insights into leaching behavior, as it provides information on possible solubility controlling mineral phases although the above framework provides the specific basis only for evaluation of inorganic constituents. A program has created that changed the input file of MINTEQ (version 3.2), based on the change of the variables. Zinc has effective result by adjusting the pH between 6 and 10 with 7 and 90 days of curing. Maximum stabilization of Iron has found at pH 6 with less effect of curing days. Curing age was not significantly affected chromium leaching. Copper and iron are in the high amount, which leached more than other metals. Cu metal is not detectable in Cp & Sp samples after 7 days curing. Ni metal is below detectable limit in Cp, Sp, Fp & Lp samples. The model was run with different combinations in order to be able to determine the effect the alterations of pH. The computed results showed that increasing the addition of alkaline binder is more effective to improve the stability of heavy metals in matrix. Alkaline pH values can increase the solubility of heavy metals very less as compare to acidic pH.
Statistical analysis plays an important role in the prediction of results and correlation between parameters. This statistical analysis was determined by two ways: Univariant analysis, Multivariate analysis.

Univariant statistical analysis is appropriate technique to find out the correlation between two parameters. Regression analysis can be used for any type of relationship. Degree of relationship between two variables is presented by the means of correlation coefficient ($R^2$). All samples show the highest correlation with pH 2. The highly correlated metals are Fe & Zn at different curing days. Nickel metal, anion and cation species showed lowest correlation. Correlation coefficient has increased in following order Ni>Cr>Cu>Fe>Zn. There is a perfect linear relationship between all the sample and 7 days of curing. The emphasis in factor analysis is to describe the covariance among variables in terms of a few underlaying unobservable random quantities or factors. Varimax rotation is used for the factor analysis because this method attempts to make the loadings either large or small to ease interpretation. The data appear normal no outliers are apparent. 1, 2 & 3 factor accounts highest variability in data, 4 - 5 factor shows small variability in data and 9 - 11 are likely unimportant for 7 days cured samples. Large positive loading is observed for Fe, Cu and Na for 7, 28 days cured samples respectively. Result indicate large positive loading Cp, Sp, Fp, Lp for factors, so label these factors as pure material. F1, L1, L2 have large positive loading for factors (Table 1), so label these factor as developed concrete (containing maximum fly ash and sludge).

Chapter 5 focused on the long term stability, leaching and fulfill the mandatory requirement by performing the TCLP test. It is divided into three parts:
Environmental stress condition is discussed in part “A” (long term stability): The durability of concrete refers to the extent of which the material is capable of resisting deterioration caused by exposure to service conditions. The durability of cement pastes is strongly influenced by the internal chemistry, and microstructure of mixes. The effect of environmental stress condition on the durability of screened concrete samples was assessed in terms of stability. Leachability of heavy metals also performed after durability test on the same samples of developed concrete. Heating-Thawing (HT) and Freezing-Thawing (FT) are the weathering simulation studies. In this study, 30% weight loss was used as a rejection ground after durability testing of the ratio. Wet/dry and freeze/thaw durability tests showed up to 10% weight loss after 12 cycles. The developed products when subjected to heating thawing process withstand all 12 cycles. The results obtained in this study proved that extensive cure times favorably increase the durability of the treated waste, thus a 28 & 90-days curing was determined to be the most effective in the S/S application. Weight loss from the freeze/thaw durability test ranged from 0.37 to 0.98% and heat-thaw durability test ranged from 0.28 to 0.42% after 4 cycles. L1 and L2 concrete samples (Table 1) were soiled during FT & HT durability test. Strength of these two samples was very low as compare to other samples. FT was found to be more deteriorating as compared to HT.

Short term leaching test (Available NEN-7341) was performed on the samples after durability test, to assess the effect of HT and FT cycle on metal fixation. Only Fe, Cu, Zn, Ni and Cr were in the detectable and these metals also in the limit of hazardous waste management rules, 1986.
Potential long term diffusion leachability indexing is explained in part “B”: Long term leaching test (64 days) is used as tool to estimate the release potential of constituent from waste materials over a range of possible waste management activities including during recycling or reuse. The leaching procedure was based on the Dutch diffusion leaching test NEN 7345. Results are usually interpreted by using log release (mg/m²) vs log of time. pH of samples was in the range of 9.1 - 7.7 whereas electrical conductivity was 12.7 - 9.2. Result shows that chemical processes occurring during water solidification decreases the availability of nickel, lead and manganese. Iron release decreased with increase in waste/binder ratio. The leaching mechanism show low leaching of copper and zinc than iron. The effective diffusion coefficient also called as Leachability Index. The order of fixation of metals on the basis of their leachability index is: Fe>Zn>Cu>Cr>Ni>Mn.

In part “C” regulatory requirement of developed concrete is fulfilled through TCLP test: Solidification/Stabilization is a common practice for the treatment of waste containing heavy metal before they can be disposed of in a secure landfill or reuse. In order to determine toxicity, the USEPA has established the Toxicity Characteristic Leaching Procedure (TCLP) designated as SWLT Method, a procedure intended to produce a leachate comparable to what would be leached by the material in the environment. The leachates (before and after treatment) were analyzed for heavy metals. Different compositions of fly ash and hazardous waste were tested for its leaching behavior. It is concluded that up to Lp (Table 1) combination were successfully stabilized accomplishing minimum leaching of heavy metal below TCLP limit with maximum compressive strength. After treatment only Iron, Copper and Zinc metal was found in leachate. The Mn, Ni and Pb metals was below the detection limits after treatment in
leachate. In order to treat metals like Fe, Zn, Cu successfully to meet the TCLP limit of 10 mg/l.

Finally, the cost benefit analysis has performed in chapter 6. Solidification/Stabilization (S/S) has proven to be a cost-effective treatment technique for managing hazardous waste materials in development concrete.