8.1 Overall view of the problem

Ferrochrome industries face the problem of disposal of the waste ferrochrome slag because of appreciable residual chromium content in it. Leaching studies indicate the chromium release from the slag very often exceeds the regulatory norms causing the chromium pollution problem. This research work was undertaken with a view to finding the solution to Ferrochrome slag disposal problem and to explore its utilization potential.

8.2 Major Research Activities undertaken

The research work was carried out in following five broad areas closely interlinked to one another.

- The Characterization study of Ferrochrome slag was undertaken to evaluate its physico-chemical, mineralogical and microscopic properties, with a view to analysing the chromium oxidation state in the slag and assessing the suitability of the ferrochrome slag as reusable material.

- Elaborate leaching study was carried out to assess the chromium leachability from the slag matrix.

- Chromium immobilization study was undertaken to analyse the inherent chromium immobilization mechanism in the slag and the performance of chromium immobilization in cement matrix.

- Experimental work was undertaken to evaluate the suitability of Ferrochrome slag for its use as concrete aggregate.

- Modelling study was carried out to analyse the factors and processes responsible for chromium leaching from Ferrochrome slag.
8.3 Characterization study of Ferrochrome slag

From the results of various Characterizations studies of FeCr slag, it is concluded that

- Both Air cooled lumped slag and water cooled granulated slag as available in the industry is found to possess good mechanical and engineering properties so that they can be gainfully utilized as construction material.

- From the chemical characterization study, the ferrochrome slag is found to contain the major chemical species like Alumina, Silica and Magnesia along with significant quantities of environmentally harmful Chromium compounds whose leaching from the slag matrix causes chromium pollution problem.

- The mineralogical characterization of Ferrochrome slag by X-ray Diffraction (XRD) study indicates the presence of dominant mineral phases like Partially Altered Chromite (PAC), Mixed Spinel (MgO.Cr₂O₃.Al₂O₃), Enstatite (MgFeSiO₄), and Fayalite (Fe₂SiO₄). Significant amounts of chromium as metallic (Cr, Fe)₇C₃ phase is found to be present in the form of globular, elliptical and dendritic grains.

- Microscopic studies of FeCr slag analyses the structural aspects of three main phases like (i) Ferrochrome Metallic phase (ii) Oxide type mixed Spinel phase (iii) Silicate phases. Globular and lath shaped ferro-chrome metal are visible along the intergranular spaces of silicates. The oxide spinel phase is seen as euhedral grains. Silicate phase is found to be mostly elongated and lath shaped. The Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy study estimated the chromium content ranging from 0 to 45 % in spinel phase followed by 18% to 36 % in metallic phase and 1 % to 12 % in silicate phase.

- From the mineralogical & microscopical characterization studies of the ferrochrome slag samples, it is concluded that residual chromium in the ferrochrome slag mostly remains immobilized as Cr (III) in highly stable mixed spinel phases like Chromite /Magnesium Aluminium Chromite and thereby inhibiting significant chromium release from the waste slag.
8.4 Chromium Leaching from Ferrochrome slag

From the various Chromium Leaching Study results the following important conclusions are drawn.

- Considerable amount of Total chromium of 28464 to 35477 mg/kg is found in the ferrochrome slag whereas highly mobile and toxic Cr (VI) is found in the range of 6.5-12.8 mg/kg which is only of 0.023 to 0.036% of the Total chromium. This indicates almost all the chromium present in the slag is in the form of less mobile Cr (III) and metallic form.

- Availability as a screening test provides an assessment of the maximum potential for chromium release from the ferrochrome slag. The Availability of chromium is found within the range of 1.66 to 2.58 mg/kg for Cr (VI) and 24.7 to 31.4 mg/kg for Total Chromium (TCr). Availability values are found to be only 20.1 to 28.9 % of total Cr (VI) content and 0.088 to 0.097% of Total chromium.

- Chromium solubility and release as a function of Liquid to Solid (LS) ratio as a screening test provides an assessment of the maximum potential for release without consideration of the time frame for release to occur. Maximum chromium release of 2.88 mg/kg is found to occur at LS ratio of 10.

- Characterization leaching tests with Chromium solubility and release as a function of pH were carried out in the pH range of 4-11. The Chromium solubility is found to be minimum in the intermediate pH range of 6-10. The solubility considerably increases with decrease in pH because of dissolution of chromium compounds.

- The regulatory TCLP study results of leachate chromium values are found to be in the range of 0.076 to 0.158 mg/l for Cr (VI) and 0.58 to 1.12 mg/l for total Cr. The TCLP results for toxic Cr (VI) very often exceed the Indian discharge standard causing chromium pollution problem.

- The leaching study results indicate that the chromium release is not affected by temperature. This result is expected as the ferrochrome slag is formed in very high temperature condition in furnace.
8.5 Chromium Immobilization Mechanism

From the results of Immobilization studies, the following important conclusions are drawn.

- Even though the ferrochrome slag samples contain considerable amount of residual chromium, regulatory TCLP results show very small chromium concentrations (0.58 to 1.12 mg/l) in the leachate.

- The binding efficiency of chromium was estimated by means of an empirical formula of Factor Sp developed by FEhS institute in Germany [84, 85]. The high Factor Sp values of slag samples vindicate the very low chromium leaching from the slag. The chemistry, mineralogy and microstructure of the chromium species in slag are found to strongly immobilize them in the highly stable spinel strictures and preventing their release from the slag.

- The TCLP test results from cement paste cube specimens with dissolved salts of chromium show the encouraging results with respect to chromium immobilization in cement matrix. The results indicate that while Cr (III) is well immobilized in all types of cement matrix, Cr (VI) is not suitably fixed in Ordinary Portland Cement (OPC) and fly ash based Portland Pozzolana Cement (PPC). But the slag based Portland Cement (PSC) has been found to be most effective in immobilizing Cr (VI) as well as Cr (III). The reason may be that, the sulphide and ferrous content in the slag first reduces leachable Cr (VI) to Cr (III) and then the same becomes well immobilized in the cement matrix.

8.6 Ferrochrome Slag as Concrete Aggregate Material

- Air cooled Ferrochrome slag after material recovery as available in the size range of 8-20 mm and is found to possess good aggregate properties such as crushing strength impact strength, abrasion resistance. Therefore the air cooled slag can be used as coarse aggregate in concrete. Water cooled granulated slag is found to possess the desirable technical properties for its use as fine aggregate in concrete work.

- Fresh concrete test results of concrete with Ferrochrome slag as aggregate material show medium workability with slump values lie in the range of 30-40 mm.
Hardened concrete test results show that concrete with air cooled Ferrochrome slag as coarse aggregate shows a 19-21 % increase in compressive strength, 5.7-6.5 % increase in flexural strength and increase 5.2-6.3 % in split tensile strength with all types of cement as compared to concrete with natural stone as coarse aggregate. This good result is attributed to the better aggregate properties of ferrochrome slag and indicating the suitability of the slag in high strength concrete application [142].

Concrete with Ferrochrome slag as fine aggregate shows similar results as compared to concrete with natural sand as fine aggregate. This indicates that the granulated slag can be used in place of sand.

Compliance test with Short tank leaching tests were carried out on the concrete specimens with different types of cements having varying percentage of FeCr slag as aggregate with distilled water at a pH 6.68 and with TCLP extraction liquid at pH 2.88. The results of Cr (VI) and total Cr concentrations in the leachate are found to be in the range of 14 to 34 and 16 to 42 µg/l respectively, which are well within the US EPA and Indian discharge standards. Concrete with slag based cement PSC show the minimum chromium leachability, because of its reduction ability to convert leachable Cr (VI) to insoluble Cr (III). 64 days cumulative leaching results of chromium in leachate are found in the range of 4.8 to 9.6 mg/m² well within the international building material protocol like BMD-1995.[15] From these results, it is inferred that the service life of concrete is not likely to create environmental pollution problem, indicating the environmental compatibility of ferrochrome slag as concrete aggregate material.

8.7 Modelling the Chromium Leaching

From the modelling results of long term chromium leaching from the unbound and concrete bound ferrochrome slag, the following inferences may be drawn.

Long term chromium leaching from ferrochrome slag was carried out for 750 days with leachate renewals at the prescribed time intervals. After an initial high value, the Cumulative amount of chromium leached is found to increase linearly with respect to cumulative time (t) till 150 days. After that the rate of leaching is found to decreases finally reaching a constant value towards the end of 750 days, indicating depletion of
leachable of Chromium from the slag. The result is in good agreement with the previous work [23].

- The long term leaching (150 days) modelling equation for Cumulative amount of total chromium leached from FeCr slag is found as $T_{Cr} = 142.1 + 153.8 \cdot t^{0.5}$, here the initial surface wash-off term comes out to be $142.2 \mu g/l$.

- The long term leaching (150 days) modelling equation for Cumulative amount Cr(VI) leached from FeCr slag is found as $Cr(VI) = 48.28 + 46.9 \cdot t^{0.5}$. Here the initial surface wash-off term comes out to be $48.28 \mu g/l$.

- It is concluded from the long term chromium leaching modelling results that, diffusion is the principal mechanism with an initial surface wash off.

From the Modelling Results of Full Factorial Design of Experiments [19], the following key physico-chemical Factors are found to affect chromium leaching from ferrochrome slag.

- The Linear Regression equation for leaching of Cr(VI) is obtained as
  
  $Cr(VI) = 1007.5 - 330 \cdot pH - 560 \cdot Size + 235 \cdot Time + 212.5 \cdot pH \cdot Size - 202.5 \cdot pH \cdot Time - 97.5 \cdot Size \cdot Time + 155 \cdot pH \cdot Size \cdot Time$.

- The Linear Regression equation for leaching of Total Cr is obtained as
  
  $T_{Cr} = 3901 - 526 \cdot pH - 2324 \cdot Size + 1211 \cdot Time + 199 \cdot pH \cdot Size - 161 \cdot pH \cdot Time - 764 \cdot Size \cdot Time + 114 \cdot pH \cdot Size \cdot Time$.

- Both Cr(VI) and Total Cr follow the similar kind of leaching pattern and are affected by the same factors in the similar manner.

- pH, Size and Contact Time as principal factors and Interactive factors are found to affect the chromium leaching from the ferrochrome slag.

- Particle Size reduction is found to be the most important factor. The leaching is found to increase appreciably with reduction in particle size.

- Low pH causes more leaching because of dissolution process.
Increase in contact time increases chromium leaching from the slag and then remains practically remains constant after 7 days.

Modelling Results of 64 days Tank Leaching test[7] for concrete specimens show that Square root of Cumulative Time vs Cumulative Chromium concentration plots are found out to be straight line($R^2$ values more than 0.98) with slope values close to 0.5 indicating diffusion is the principal leaching mechanism from concrete bound slag specimens. High Leachability Index(LI) values from the graphs (more than 12.5) vindicates the experimental findings of very low level chromium mobility from all the concrete specimens.

8.8 Over all Conclusion

The ferrochrome industries presently face the disposal problem of its major waste ferrochrome slag because of chromium leaching from the slag. From this research work, it is concluded that, the ferrochrome slag, can be suitably utilized as concrete aggregate material with chromium immobilization in cement concrete matrix without causing significant environmental pollution problem.

8.9 Significance of this research work

This research work was taken up to solve a live problem of disposal of ferrochrome slag by the concerned industries. The satisfactory outcome of this work will contribute in the following manner.

The present study has found the simple and effective ways to solve the problem of the disposal of ferrochrome slag. The ferrochrome slag can be used as concrete aggregate by the industries or by the local the entrepreneurs thereby reducing the use of natural resources causing environmental degradation. In this sense ferrochrome slag can be considered as green concrete material.

The utilization of ferrochrome slag will not only eliminate the cost of its disposal but also it will contribute to value addition.
As per my extensive review of literature, there are very few research work carried out on ferrochrome slag. Elaborate environmental study on ferrochrome slag has not been attempted elsewhere.

8.10 Scope for further research work

This research work has achieved the principal objective of finding the solution to the disposal problem of Ferrochrome slag. The end result comes out to be satisfactory in the sense that, while finding the means for immobilization of leachable chromium for disposal purpose, the slag comes out to be a good concrete aggregate material. Here in this research work major emphasis was on the environmental solution of ferrochrome slag. But it opens up for following further research work in this area.

- Taking lead from the better strength related results of the concrete with Ferrochrome Slag as coarse aggregate in the present research work, further research may be carried out for the utilization of Ferrochrome Slag in high strength (M-50 & higher) concrete work.

- Workability is found to be medium. Further study should be carried out to improve workability with the use of different super plasticisers and admixtures.

- Durability study should be carried out to assess the long term performance of the concrete with Ferrochrome Slag as aggregate material.