MÖSSBAUER STUDIES OF MATERIALS USED TO IMMOBILISE INDUSTRIAL WASTE

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Today's society produces toxic wastes ranging from nuclear wastes, with various levels of activity, to incinerator ashes such as sewage sludge ash which contains harmful heavy metals. The harmful nature of some components of these wastes means that safe immobilisation can be necessary. Methods have been, and are being, developed to immobilise these wastes. Vitrification is used in the UK to immobilise high level liquid waste (HLLW) from nuclear fuel reprocessing. The study and development of suitable methods and materials to immobilise waste is the focus of the work reported in this paper. ^{57}Fe Mössbauer spectroscopy has been used during these studies to identify the valence state and coordination of iron in glasses and ceramics.

A material designed to immobilise waste requires structural stability, compositional flexibility, thermal stability and chemical durability. Optimum properties are obtained by modifying the composition and production parameters of glasses and ceramics.

UK high level waste (HLW) borosilicate glasses have been studied to determine the effects of Fe_2O_3 addition on glass chemical durability, thermal properties, density and redox [1]. Results indicated that 5–10 wt% Fe_2O_3 addition provides optimum improvement in chemical durability. ^{57}Fe Mössbauer spectroscopy revealed Fe is in these glasses as Fe^{3+} ions in tetrahedral coordination, strengthening the glass network through increased network polymerisation.

Also ^{57}Fe Mössbauer spectroscopy has been widely used to study iron-containing phosphate glasses to investigate the redox and structure [2]. The particular attraction of these glasses is their combination of low melting temperatures and high chemical durability. Extensive studies have been performed [3] on the doping of iron-phosphate glasses to improve the properties that make them suitable for waste immobilisation. We have shown that modification of these glasses by a number of components substantially improves physical properties. However, interestingly, ^{57}Fe Mössbauer spectroscopy has shown that such modifications produce only small changes in Fe coordination and in Fe^{2+}/Fe^{3+} redox ratio. Therefore the iron in these glasses is relatively immune to compositionally-induced changes in these glasses [4].

Vitrification is being considered as a possible technology for safe disposal of toxic waste streams such as sewage sludge combustion ashes (SSA), since vitrification of such waste is becoming more economically viable due to higher landfill costs and stricter legislation. ^{57}Fe Mössbauer spectroscopy has been used [5] to determine the coordination of the Fe in the glass. The glass composition has been modified to improve the glass forming properties of the waste and the potential of the glass to be used in another application.

Alternative energy efficient methods of vitrifying waste such as dielectric heating have also been investigated. The effect of internal heating, choice of precursor, local atmosphere, and melt time on the iron redox in iron phosphate glasses has been investigated by ^{57}Fe Mössbauer spectroscopy. Short melt times coupled with reducing local sample environments have enabled homogeneous glasses to be formed with significantly higher Fe^{2+}/Fe^{3+} redox ratio than the corresponding conventionally melted glasses.

Ceramics are an alternative option to vitrification for the immobilisation of actinide rich waste streams where iron (and other transition metals) may be present either as a component of waste stream or added for the purpose of charge compensation. Iron valence, coordination and site partitioning in a number of proposed and novel ceramic systems have been investigated by ^{57}Fe Mössbauer spectroscopy.

Vitrification is also being considered for immobilising some "legacy wastes" that are by-products of the UK's early nuclear power programmes. These wastes are often present in relatively small volumes and may be chemically diverse and poorly characterised. They include several wastes that are rich in the problematic actinide plutonium.

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