TecEco: Cements Based on Magnesium Oxide

F. P. Glasser

1. Background

The writer of this report, Professor Fredick Paul Glasser of 26 Gilbert Road, Bucksburn, Aberdeen, Scotland, is the holder of a PhD (Pennsylvania State University) and a DSc (University of Aberdeen). He is a Fellow of the Royal Society of Edinburgh, an Academician of the Academy of Ceramics and a Fellow of numerous other learned Societies. He is the author or co-author of more than 400 published in peer-reviewed Journals, as well as several book chapters, etc. Many of these relate to the production and use of inorganic cements.

Professor Glasser was approached by TecEco for an independent evaluation of their proprietary developments. In this capacity he has received both confidential and non-confidential material from Mr John Harrison. The following evaluation and appraisal is based on Professor Glasser's knowledge of developments in the field of cementitious materials as well as information received from TecEco. The report makes use of confidential and proprietary information but such information is not reproduced in this report, which may be freely communicated. Its contents may be reproduced or quoted in context provided acknowledgement of source is made.

2. Present Status of Cement Production

Several types of inorganic cements are made commercially. Overwhelmingly, Portland cement production dominates. Most technically advanced countries produce 200 – 400 kg per head of population per year: perhaps more in emergent countries, e.g., China. The high rate of production makes substantial environmental impacts (quarrying, pyroprocessing with gaseous and particulate emissions), consumes much fuel, mainly low-grade coal, and ties up vast capital investment in plant and transport. The science and technology of Portland cement production are well understood with the result that the process operates at nearly the optimum efficiency: small incremental savings remain to be made as old plant is replaced by new, but as this process approaches completion, little further scope exists for improvement.

Yet the industry has come, and will come, under severe pressure to reduce its specific energy inputs. Various responses are possible, for example, cement can be supplemented by other materials including iron blast furnace slag and coal combustion fly ash. The Battelle Foundation is presently engaged in a desk study of the options available to the industry: the writer is one of a number of experts who will review their provisional findings in September, 2001. It is however apparent that only limited scope for betterment exists and that a range of more radical options for change must also be considered.

To sum up the present situation, the built infrastructure relies on Portland cement. It is a well-specified product, widely available and relatively cheap. When used according to codes of good practise, it is a satisfactory product. Yet drivers for change exist. These are mainly concerned with high fuel expenditure and high emissions of carbon dioxide, sulfur and nitrogen oxides associated with production.

3. The TecEco Development

3.1 Introduction

The TecEco developments are described under the following headings. A very brief overview is followed by descriptions of economics, technical proof of concept, market acceptance and relevant environmental considerations.

3.2 Overview

TecEco have developed cements based on magnesium oxide. Magnesium is an element abundant in nature, although the preferred starting material, magnesite, $MgCO_3$ is less widely distributed. Suitable raw materials are readily identified and easily extracted by straightforward quarry operations.

A number of permutations based on magnesium oxide and which lead to practicable formulations are described in Table 1. The Table also includes my specific comment on the prospects for patentable developments.

Table 1: MgO-Based Cements

Other materials added to and activated by MgO	Comment on the product obtained.
Concentrated aqueous $MgC\ell_2$	Sorel cement. First developed in mid 19^{th} century. Unlikely to be patentable. Not recommended for further development.
Concentrated aqueous $MgSO_4$	Sulfate containing analogues of Sorel cement. Same comment applies.
Solid and aqueous phosphates	As above. Phosphate is expensive, so applications will be confined to special cements, e.g., for tile setting.
Coal combustion fly-ash, iron blast furnace slag and other waste products, including calcined clays.	Most practicable of all the alternatives proposed. Embraces the "geopolymer" compositions. Room for innovation and scope for patent protection. See text.
Mixtures of MgO-based materials with Portland cement: ternary blends of MgO/Portland/supplementary cementing materials.	Portland cement provides comfort to civil engineers while diminution of Portland cement content secures improved energy efficiency. Patentable. See text.

3.3 Economics

Economics are scale-dependent. There is need for a proper evaluation, probably coupled with pilot plant trials with careful economic costing. There can be little doubt that where suitable resources exist locally, so as to minimise transport costs – especially land transport – MgO based cements could have a significant economic benefit. Both Portland (calcium oxide based) and magnesium oxide based cements require pyroprocessing. Relative to Portland cement, significant cost reduction in making MgO-based products arises from:

- Energy savings in pyroprocessing; energy requirements are less for MgO based materials than for CaO-based equivalents.
- Capital investment in pyroprocessing equipment. Lower temperatures minimise need for expensive and massive refractory-lined kiln constructions.
- Lower energy for grinding. Some 10% of the energy required for Portland cement production is expensive electrical energy consumed in grinding the indurated "clinker". Lower firing temperatures for MgO-based materials substantially reduce this requirement.
- No other stages which require extra energy inputs, relative to Portland cement, have been identified.

Significant environmental advantages thus accrue from lowered emissions at each stage of manufacture except quarrying and transport, which are comparable to OPC.

3.4 Technical Proof of Concept

With the limited resources at their disposal, TecEco have demonstrated that products based on magnesia are:

- Simple and flexible in terms of formulation.
- Have adequate fluidity and workability time prior to set.

- Develop adequate compressive strengths as a function of time.
- Not affected by common aggressive environments and indeed, may be improved as a consequence of reaction with atmospheric carbon dioxide.
- Ecologically more satisfactory than Portland cement.
- A technological product capable of being implemented under typical industrial conditions, using methods and equipment borrowed from operations which normally use Portland cement.
- Compatible with typical mineral aggregates, fibres and steel.

At the same time, a number of technological issues concerning magnesia-based formulations have been addressed only in part. Amongst these are:

- The long-term dimensional stability.
- Resistance in the long-term to climatic variations, e.g., wet/dry cycling, freeze-thaw and combined impacts.
- Creep under load.
- Corrosion potential for embedded steel, particularly in the presence of chloride ions.
- Porosity/permeability relationships.
- Performance of blends of MgO with other cheap supplementary cementing materials, e.g., coal combustion fly ash, iron blast furnace slag.
- Optimisation of type and amount of blending agents.
- Heat output and maximum temperature attained during early hydration.
- Long-term fate of unhydrated clinker and potential adverse impacts on performance.
- Fire resistance and thermal dilational coefficients.

4. Market Acceptance

The building materials industry is intensely conservative. Innovation is the exception, not the rule. Nevertheless, a sharp distinction needs to be made between structural and non-structural applications. Thus a novel cement material might be acceptable for kerbstones (non-structural) but not for structural load-bearing lintels of similar dimension. Indeed, TecEco have thus far been most successful in undertaking semi-commercial production of non-structural shapes.

This suggests that the way forward is, initially to market non-structural shapes: for example, pavers, slabs, panels and cladding, fencing, tiles, etc. This ensures cash generation with which to finance ongoing development. A business plan has been developed but not reviewed by the writer which, it is understood, anticipates a staged development.

My recommendation is that short term development should concentrate on cements based on MgO, on blends of MgO with Portland cement and 'ternary' blends of magnesium oxide-Portland cement-aluminosilicates: see Table 1. The preferred aluminosilicate materials are those which react pozzolanically with the alkaline activator – in this instance mixtures of magnesium oxide with Portland cement - or with MgO, should that prove to be an acceptable activator. These formulations would be marketed in the first instance for non-load bearing building components.

5. Environmental considerations

It is difficult to foresee the exact direction of future environmental policy. Environmental priorities are often dictated at least in part by emotional and political considerations rather than sound scientific advice. Nevertheless, environmental action groups have considerable and increasing influence on policy. I can only comment on the rational considerations. Whatever view one takes of current priorities, it is inevitable that the cost of energy will continue on an irregular but rising trend: government will respond using direct regulation as well as tax policies which penalise energy-intensive operations and promote energy saving. This suggests a positive and favourable climate of acceptance for magnesia-based products.

Moreover, whole-life and re-use or recycling are likely to assume increasing importance. Portland cement materials are inherently difficult to recycle as very high temperatures are required to regenerate their cementitious potential of recycled material. Intuition suggests that MgO-based cements should have better potential for recycling. If MgO-based cements were demonstrated to be readily regenerated - and such a demonstration would not be difficult - this could contribute substantially to their environmental acceptability and long-term economics associated with achieving "sustainable" production. Moreover, the durability of MgO-based products is often improved by carbonation. Provided carbonation is an integral part of manufacture, i.e., carbonation occurs within the "factory gate" net CO_2 emissions associated with manufacture will be greatly reduced relative to Portland cement.

6. Summary

MgO based cements represent one of the few recent advances in inorganic cements which are suitable for large volume production. They are capable of commercialisation. TecEco have limited resources but have done much valuable groundwork in support of their innovation. This includes actual transfer to the plant, by achieving small production runs. This greatly reduces the risk that unexpected problems will arise in transferring technology to actual production.

Production experience is seen as providing comfort both to the inventors and prospective investors. Steady market penetration will enable cash flow to be generated and the resulting revenue stream can be used to support ongoing R and D. In the meantime, monitoring of in-service product performance can be used to establish marked opportunities, build confidence amongst prospective users and specifiers and permit products to be licensed for load-bearing applications.

TecEco's R and D has been deployed over a large number of potential products. The time to focus has now arrived. Based on payback time and prospects of success, my evaluation of the lead areas for study are:

- Laboratory trials and pilot plant production of carbonated products based on magnesium oxide/hydroxide and supplementary cementing materials, with ongoing R and D support.
- Laboratory trials and pilot plant production of composite cements based on Portland cement – magnesium oxide/hydroxide compositions with and without supplementary cementing materials.
- Further technical development of carbonated products, also including energy audits.

It would be intended to develop products intended in the first instance for non-structural applications. The extension into load-bearing materials, particularly intended for tensile and flexural loadings, should also be pursued using glass-fibre reinforcement. A further area for medium-term opportunity is therefore:

- Development and testing, supported by R and D, of the durability and ageing behaviour of glass-fibre reinforced magnesium hydroxide-carbonate matrices.

Finally, to sustain the introduction of magnesia-based cements into the market place, it will be necessary to undertake a further R and D task:

- Determine compatibility of magnesia based components with other commonly-used constructional materials: steel, aluminium, copper, tile, brick, gypsum and wood: also with commonly used decorative protective coatings such as paint and galvanised finishes
- Work towards a national specification governing the composition, production and use of MgO-based cements. At present, and depending on country, building codes are in transition between prescriptive and performance-based specification. Nevertheless, consumer acceptability would be greatly assisted by having an appropriate specification arising as a consequence of independent peer review.

Comments and queries on this report may be sent to the writer at f.p.glasser@abdn.ac.uk. The opinions expressed here are entirely those of the writer.

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