Towards greener pyrotechnics

Prof Walter W Focke, Ollie del Fabbro, Cheryl Kelly, Kolela Illunga, Thilo van der Merwe, Elmar Muller and Maria Atanasova

Green chemistry is an initiative adopted by chemists and chemical engineers striving towards the sustainable manufacture of chemical products. It is a philosophy that encourages the design, development and implementation of chemical products and processes that reduce or eliminate the use and generation of substances that are hazardous to the environment and to human health. Green chemistry for pyrotechnics is currently an intensive global research effort.

AEL Mining Services, a leading developer, producer and supplier of commercial explosives, initiating systems and blasting services for mining, quarrying and construction markets in Modderfontein, is also committed to this ideal. It has made significant progress in developing green chemistry pyrotechnic systems and manufacturing methods. As part of its efforts in this regard, it has partnered with the Institute of Applied Materials (IAM) at the University of Pretoria.

The main focus of this research collaboration over the last 10 years was to find greener alternatives to lead- and other heavy metal-based compounds currently in use in shock tube detonators. This includes lead-based primary explosives, as well as lead-based delay compositions.

The National Research Foundation (NRF) has also supported this research through its Technology for Human Resources in Industry Programme (THRIP). While the research was primarily of an academic nature, it has led to several patents in addition to numerous scientific publications, conference contributions, and master's and bachelor's research dissertations. Many students' studies received generous financial support from AEL Mining Services. Selected students have also excelled by winning innovation awards for their research.

Pyrotechnics

A conventional pyrotechnic composition is a mixture of a metal fuel and an oxidiser that is capable of a self-sustained exothermic redox reaction. The reaction results in the oxidation of the metal to form a more stable oxide and the reduction of the metallic oxide to the free metal. The thermite reaction between aluminium and iron oxide powders is a popular example. This reaction generates temperatures that exceed 2 000 °C as the aluminium is oxidised to alumina and pure iron metal is formed. Pyrotechnics find widespread use in civilian, military and mining applications, generating sound, light, smoke and high heat. The commercial detonators used in mining and quarrying depend on pyrotechnic compositions for the exact timing of sequential blasting events. This is achieved by the highly reproducible burn rates of the pyrotechnic composition, which is filled into the delay element assemblies.

Ultimately, this detonator subassembly comprises an ignition source, a small-diameter tube containing the compacted pyrotechnic composition and an ignition transfer system. Following ignition, a combustion wave travels down along the tube at a constant velocity. This ensures the transmission of the initiation impulse to the detonator in a precisely adjustable time interval. The delay elements are currently manufactured by pressing the pyrotechnic composition into aluminum tubes. The automated filling and pressing process requires powders with good free-flow behaviour. At present, pyrotechnic time delay formulations are based on silicon as fuel, in combination with red lead oxide (fast-burning for short time delays) or barium sulphate (slow-burning for long time delays).

Ultimately, lead and its compounds in detonator time delays must be phased out owing to environmental and health concerns. The AEL team has found that bismuth oxide (Bi_2O_3), prepared by thermal decomposition of bismuth subcarbonate, may provide suitable fast-burning compositions with silicon as fuel (155 mm s^{-1} with 20% Si). Alternatively, the Si-Sb_6O_{13} system yielded slow-burning compositions that could be slowed down even

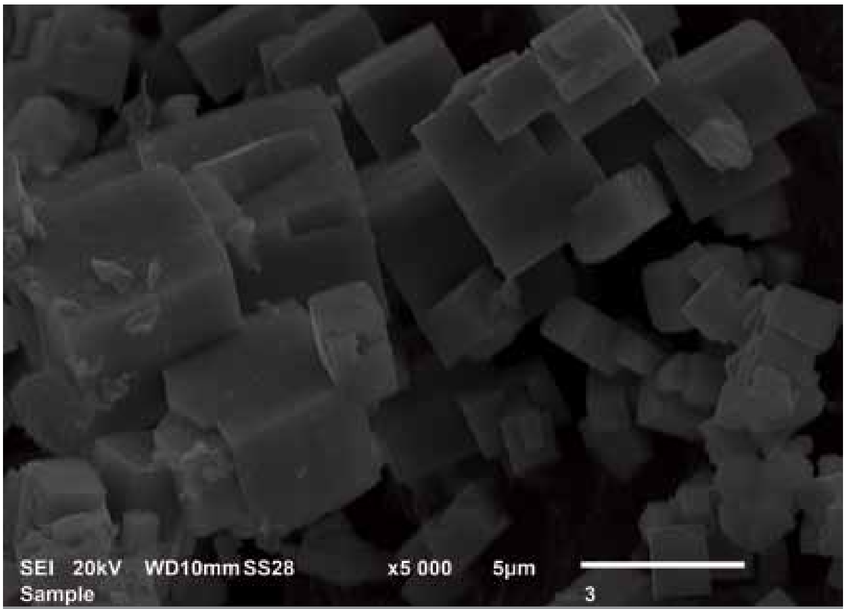

Figure 1: Scanning electron micrograph of copper antimonite crystal produced by the "green" synthesis process invented by the AEL team

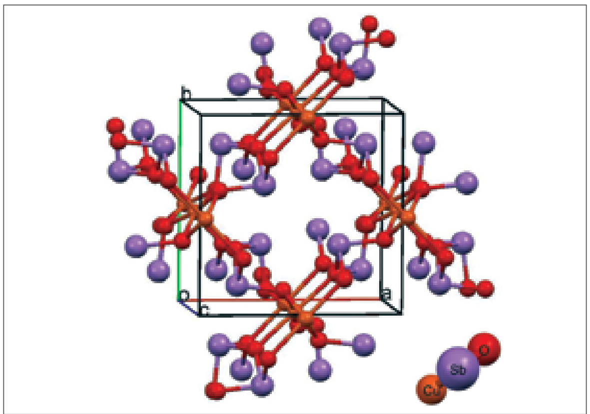

Figure 2: The $CuSb_2O_4$ structure represented as a ball-and-sticks model

further by adding fumed silica: a composition obtained by adding 10% fumed silica (add-on basis) to a 10% Si–90% Sb_6O_{13} composition that still burned reliably at a burn rate of 2.3 mm s^{-1}.

Early on, a novel oxidant, copper antimonite ($CuSb_2O_4$), was identified as a candidate oxidant for use in time delays for mining detonators with desirable properties. The AEL team recently developed a "green" effluent-free process for the synthesis of this compound. The process yields small well-formed crystals, with a cuboid habit as shown in Figure 1. The crystal structure of this material was recently determined via modelling of the powder X-ray diffraction data and confirmed via molecular modelling and Raman spectroscopy. It is evident that this material has a highly unusual crystal structure, as seen in Figure 2. Only half of the crystal positions available for the copper atoms are essentially occupied. This explains the insensitivity of compositions based on this oxidant to accidental ignition by friction and impact.

Thermites are pyrotechnic compositions that undergo reactions that are extremely exothermic and run with self-sustaining oxygen content. The energy density of some stoichiometrically balanced thermites is comparable to that of conventional high explosives. Recently, it was discovered that thermites comprised of nano-sized powders can generate temperature shocks capable of initiating high explosives. Unlike the lead-based primary explosives, they are relatively insensitive to friction, shock and electric spark. Consequently, much effort is expended worldwide to explore the use of thermites as replacements for primary explosives.

Thermite reactions are difficult to start, as they require very high temperatures for ignition. For example, the ignition temperature of the Al-CuO thermite, when comprising micron-sized particles, is ca. 940 °C. The IAM team has discovered that the ignition temperature can be significantly reduced when the binary Si–Bi_2O_3 system is added as sensitiser. Although even lower ignition temperatures are possible when the reagents are nano-sized powders, the AEL team has found that this system is capable of initiating high explosives even when the particles are only micron-sized.

Dry mixing of pyrotechnic powders is a hazardous operation. AEL has recently commercialised the much safer slurry spray-drying technology. This innovative method yields free-flowing granules, as it creates almost perfect spherical particle agglomerates. In addition to the acceptable flow properties, this process also yields well-mixed compositions from dispersions containing different powders, and provides control over the particle size distribution of the near-spherical agglomerates. Unfortunately, the silicon powder fuel used in these compositions reacts with water, liberating hydrogen gas that poses a risk for explosion.

The AEL research team developed different ways to suppress this hydrogen generation. These include the addition of a noble ion salt, for example, copper (II) ions, to introduce a competing cathodic reaction, which is controlled air oxidation of the silicon powder before slurrying and adding organic corrosion inhibitors. It was found that silane surface modification of silicon is the most effective method for the suppression of hydrogen evolution while maintaining or even improving silicon reactivity in a typical pyrotechnic composition.

Contrary to popular belief, a form of metal rust can react with the neat metal to generate very high temperatures. Manganese dioxide powders, mixed with manganese metal powder, showed reliable burning over a wide stoichiometric range. The unusual aspect of this system is that the fuel and the oxidant share a common metal. They combine to form the more stable intermediate oxide (MnO), releasing considerable quantities of heat in the process. Investigations showed that this system is suitable for time delay applications. A major advantage is the fact that hydrogen evolution from the manganese metal in aqueous slurries can be suppressed completely.

The methods currently used for measuring the burn rates of pyrotechnic time delay compositions are destructive in nature and pose some safety risks. The AEL team recently implemented a new method. A high-speed infrared camera is used and allows the real-time recording of surface temperature profiles. In combination with a mathematical model, these can be used to infer the temperature profiles inside the element and to estimate average and instantaneous burn speeds. Figure 3 shows typical images recorded during a burn test of a new formulation in a metal tube.

The example that is described in this article shows that there is potential for further innovations from the AEL team and they look forward to continuing their fruitful collaboration with the University of Pretoria into the future.

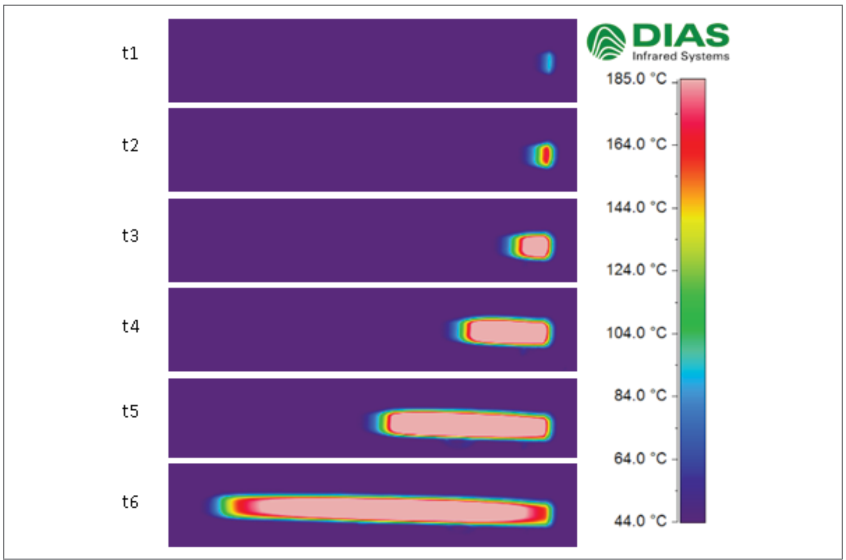

Figure 3: The progression of the pyrotechnic reaction in a metal tube as visualised by the infrared camera at various times (t1–t6) after ignition of the sample

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About the authors:

***Prof Walter W Focke**, Institute of Applied Materials, Department of Chemical Engineering, University of Pretoria*

***Ollie del Fabbro**, Institute of Applied Materials, Department of Chemical Engineering, University of Pretoria*

***Cheryl Kelly**, AEL Mining Services, Modderfontein, South Africa*

***Kolela Illunga**, AEL Mining Services, Modderfontein, South Africa*

***Thilo van der Merwe**, AEL Mining Services, Modderfontein, South Africa*

***Elmar Muller**, AEL Mining Services, Modderfontein, South Africa*

***Maria Atanasova**, Council for Geoscience*