

Andrew Fellowship Completion Report

Daniel Holland - March 2019

This report summarises my work on improving fertiliser manufacturing in New Zealand within the Andrew Fellowship. New Zealand is dependent on its primary industries, especially agriculture, and as such is a user and producer of fertiliser commensurate with its productivity. Syd Andrew had a lifetime interest in the area of fertiliser production, so this project fits within his area of interest and the wider objectives of the fellowship. The fertiliser industry in New Zealand is dominated by Ravensdown and Ballance. Both companies manufacture superphosphate here in New Zealand and import urea. Ballance also manufactures urea locally. I spoke with both of these companies early in my fellowship and they identified two key challenges for the fertiliser industry in New Zealand: (1) production of superphosphate of sufficient quality for accurate application and (2) development of more efficient nitrogen fertilisers. These two goals became the focus of my fellowship, which was supported by Ravensdown.

Superphosphate manufacturing

Superphosphate is a key product in New Zealand farming with approximately 800 kt of superphosphate applied annually. Precision application of phosphate fertilisers is desirable to minimise the risk of fertiliser entering our waterways and contributing to eutrophication. New Zealand has also attracted criticism for sourcing some of its feed phosphate rock from disputed territory in West Africa. Ravensdown and Ballance are both seeking to find ways of producing high quality superphosphate from alternative supplies of rock phosphate to mitigate these concerns. In New Zealand, superphosphate is manufactured by reacting sulphuric acid with ground phosphate rock and then immediately granulating it. There is no active drying stage in the manufacturing process which reduces costs but makes the product sensitive to the properties of the feed constituents. Furthermore, some of the production facilities are located in urban areas and some phosphate rocks evolve odorous compounds on reaction with sulphuric acid. Therefore, my work with Ravensdown has focused on three key objectives: (1) characterise the reactivity of alternative phosphate rock sources, (2) reduce the odours coming from the superphosphate manufacturing process, and (3) improve the strength of superphosphate granules.

The first objective was addressed by measuring the reactivity of a variety of phosphate rocks in the laboratory. The suitability of phosphate rocks is determined by the levels of fluoride, silica, cadmium, and iron and aluminium oxides, odorous compounds and the total P in the phosphate rocks, as well as the reactivity. In this project, the reactivity of four different rocks that potentially could be used in place of the existing supplies were tested, along with various blends of these rocks. It was found that some potential alternative rock types yielded similar reactivity to one of the existing rock sources used in the process. It is therefore possible, in terms of reactivity, to substitute between these rock supplies.

The second objective was addressed by examining the composition of phosphate rocks and odorous gases produced. Samples of the stack gas were analysed using mass spectrometry to identify any potentially odorous compounds present. This work identified a sulphur containing compounds that were a likely cause of the odours from the plant. Soxhlet extraction was used to try to identify the origin of this sulphur containing compound. Unfortunately the odour problems are intermittent and it was not possible to determine the source of the component in the small rock samples tested. Work will continue to identify the source of the contaminant and techniques to mitigate the odours produced.

Finally, we have addressed the sensitivity of the granulation process by identifying a new binder to use during granulation that will improve the strength of the resulting granules. Initial testing of the binder was performed

using fully reacted superphosphate and the resulting granules demonstrated up to twice the crush strength of granules produced without binder. It is anticipated that the binder will be less effective when using active, wet superphosphate owing to crystallisation effects that occur after granulation and the potential breakdown of the binder at the high temperature and low pH of the actual manufacturing process. Therefore, we commissioned a pilot scale plant to produce active superphosphate. In 2018 we performed our first granulation trials using superphosphate produced from the pilot plant. This work demonstrated that we could achieve a 10-20% increase in the strength of the superphosphate granules through the addition of a small amount of the binder. We will perform further trials of the new binder in the future.

Controlled Release Fertiliser

The second major project I am working on aims to improve controlled release nitrogen fertilisers. This work is looking at both improving our understanding of the release from these fertilisers and at reducing the cost of the coated fertiliser. I currently have three PhD students working in this area. The first of these has concentrated on improving our understanding of the release process. The second student is developing a numerical model of the coating process to help optimise the operating conditions of the process. The third student is developing new polymers to use as the coating material. I will briefly summarise their work here.

The first objective of the project was to improve our understanding of the release of nutrients from polymer coated fertilisers. Experimental trials of polymer coated fertilisers have shown wide variation in the improvement in nitrogen use efficiency (NUE), with some even showing that polymer coated fertilisers perform worse than conventional fertilisers. We have performed a series of tests of the release of nutrients from controlled release fertilisers in water and in the soil to help understand the reason for the variation in performance. We model the release using a diffusion model as follows:

$$J_{urea} = \begin{cases} 0 & t < t_{crit} \\ \frac{P(T)}{l} C_{sat}(T) & C_{core} \geq C_{sat}(T), \\ \frac{P(T)}{l} C_{core} & C_{core} < C_{sat}(T) \end{cases} \quad (1)$$

where J_{urea} is the flux of urea through the membrane, P is the permeability of urea through the membrane and is a function of temperature, C_{sat} is the saturation concentration of urea at the current temperature, l is the thickness of the membrane, C_{core} is the concentration of urea remaining in the granule, t_{crit} is an initial delay to the release whilst water diffuses into the core. We experimentally measured the temperature dependence of the permeability and found that it follows an Arrhenius model. With this information, Equation (1) can be integrated numerically to determine the release of urea over time. An example of the release behaviour for a commercial controlled release fertiliser is given in Figure 1 and compared with the release expected if a constant temperature is assumed[1]. The release is seen to be delayed by 2-3 weeks compared with the release expected by the manufacturer at the mean release temperature. These results show that, at least for New Zealand conditions, it is not sufficient to choose the polymer thickness on the basis of the average temperature alone. On the other hand, these results potentially demonstrate a new approach to controlling the release of nutrients to better follow the desired sigmoidal response curve by tuning the temperature sensitivity of the diffusion through the polymer.

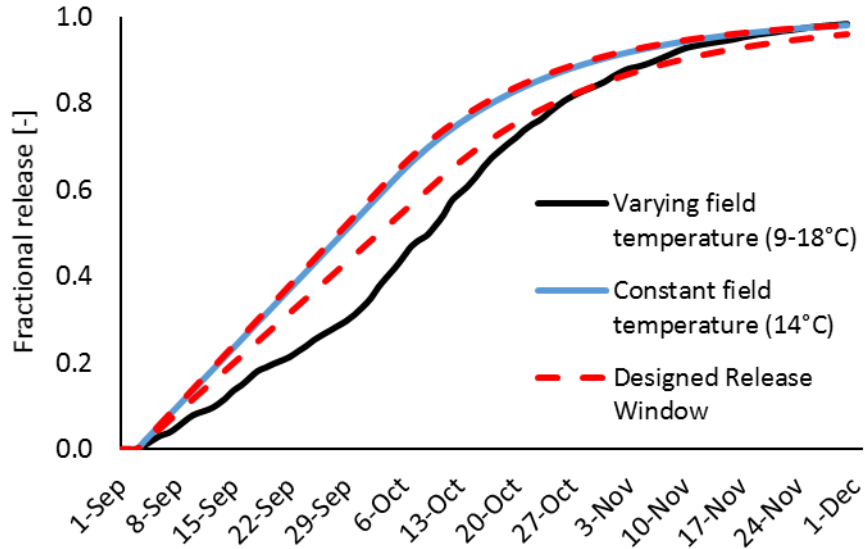


Figure 1: Comparison of the expected release rate from a controlled release fertiliser and that arising from the changing temperature in the field over the release period for a fertiliser applied in winter. The changing temperature introduces a sigmoidal shape to the release curve.

Furthermore, measurements in soils demonstrate that the supply of water to the soil and location of the fertiliser in the soil are both critical to determining the release of nutrients. Typical practice in New Zealand is to apply fertilisers as a top dressing on the surface of the soil. Figure 2 shows a comparison of the release rate for fertilisers placed on or buried in the soil when there is sufficient water (simulating irrigation) and when water may be scarce (simulating natural rainfall around Christchurch)[2]. The results demonstrate that the release rate is dramatically reduced when the available moisture is limited and that the problem is particularly significant when granules are placed on the surface of the soil. However, perhaps the most surprising result occurs in the case of buried granules with frequent, but small water application (as in the simulated rainfall case), the release rate was measured to be slightly greater than in soils where the soil remains moist throughout (simulated irrigation). We are now in the process of developing a model to describe these results. There are two factors that may contribute to the slower release rate in the soil: (1) release of urea is influenced by transport of water, and (2) accumulation of urea in the soil around the granule. We are currently developing methods to quantify these effects and determine the mechanism controlling the release.

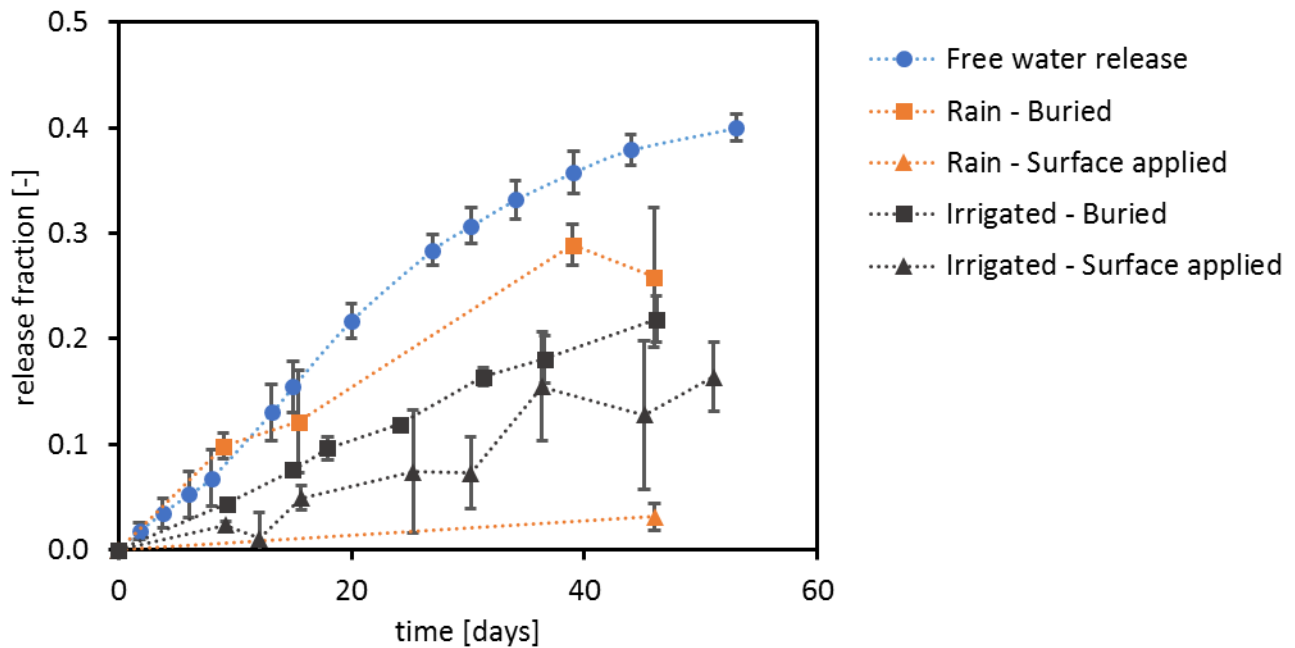


Figure 2: Comparison of the release rate from fertilisers in water and either buried in or applied to the surface of soil under conditions replicating irrigation or natural rain. All experiments were performed at a controlled temperature of 20°C using a fertiliser with an expected release duration of 150 days at 20°C.

The second objective of the project was to develop our own controlled release fertilisers. Previous work has shown that fertilisers produced in spouted bed processes are of higher quality than those produced in drum coaters, but the cost of the process is substantially higher due to the cost of heating the air used to drive the spout[3]. In the pharmaceutical industry, spouted bed coaters are probably most common. However, farmers are highly price sensitive so most controlled release fertilisers are produced using drum coating units. We hypothesised that the performance of the spouted bed process arises from the lack of contacts between particles when the spray is first applied. On the basis of this work we designed, built and commissioned a new lab-scale high intensity mixer, which it is hoped will combine the relatively low cost of operation of the drum coating process with the high quality of the spouted bed process. We have simulated the operation of the unit using discrete element modelling. In developing this model, we experimentally measured the contact properties of the granules to use in the simulation. The model was then validated using particle tracking velocimetry of dry fertiliser granules. We were able to use the model to show that it should produce more homogeneous coatings than drum coating units in a given time frame, if the operating conditions are chosen suitably. This work will be presented at the PARTEC conference in Nuremberg in April 2019[4]. We will begin lab scale testing of this coating process in 2020.

The final objective of the project was to develop new polymer materials from biological waste material to reduce the cost of the controlled release fertilisers and ensure that the polymer is biodegradable. We have developed a range of polymers from our biowaste feedstock. Using suitable polymerisation conditions, the polymers can be formed as a thin film. We are now in the process of characterising the mechanical and transport properties of these films to determine the optimum conditions to produce our coated particles. It is critical that the polymers produced are biodegradable. Many recent biopolymers have been described as biodegradable but instead they break down to produce microplastics that persist in the environment. Our bio-derived polymer still contains the complete functional group that microbes in the soil attack to decompose the natural feedstock. Therefore, it is anticipated that our biopolymer will fully decompose in the soil. An important future goal of our work will be to measure the rate of this decomposition process.

Summary

During my fellowship I have developed a new research program to address the major current challenges of the fertiliser industry in New Zealand. I have established a strong working relationship with one of the major fertiliser companies in New Zealand. To date my work has been closely tied to New Zealand manufacturers and distributors of fertilisers, however the work is relevant world-wide. To that end, at the end of my fellowship I visited Israel Chemicals Limited (ICL), the manufacturer of the pioneering controlled release fertiliser Osmocoat™.

References

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