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**Title**

Research and Development of Controlled-Release Fertilizers as High Efficient Nutrient Management Materials in China

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## **Abstract**

The use of controlled release fertilizers (CRFs) has been recognized as an efficient approach to nutrient management in China since 1997, but a critical review of the country's CRF research and development (R&D) is lacking. This contribution summarizes more than 10-year experience with CRFs and the results of an extensive review of Chinese literature on this topic. The paper distinguishes between CRFs and slow-release fertilizers (SRFs). The history of research on CRFs in China comprises three stages: 1) the exploration period; 2) the popularization period; and 3) the integration period with industrial production of CRFs. The main factors determining the effectiveness of CRFs are the coating agent's magnitude and the ratio of coating materials. The analysis of CRF development in China and other countries and of current trends and needs in agriculture allows to predict the future development of this fertilizer sector.

**Keywords:** China, Coating Agent, Coating Material, Controlled Release Fertilizer, Nutrient Release

## **Introduction**

In China controlled release fertilizers (CRFs), as a new tool in nutrient management, has received great attention since 1997 because of its high nutrient use efficiency. In the first year of the eleventh 5 year plan the Chinese government invested 50 Mio Yuan to develop CRFs and slow release fertilizers (SRFs). The purpose of this paper is to review the CRF research and manufacturing status using the authors' research results over last decade.

Nutrients controlled by coating layer outside substrate granular which is either NPK compound or urea. The coating material is solvent free resin (SFR) and coating layer formed through reaction of two to three kinds of coating materials on surface of fertilizer granular (SFR). The CRF is made by use of commercial scale fluid bed in Sanyuan Planta Controlled Release Fertilizer Company. The coating thickness, measured by metric weight of substrate fertilizer, is from 4% to 8% to produce several types of CRF with different longevity. Compound coated fertilizer is called CRF and polymer coated urea is called PCU. Nutrients release rate is determined according to Martin (1997) and Fan (2005) at normal (25°C) and high (40°C) temperature respectively. Then the structure of coating is measured by use of scanning electric microscope (SEM).

## **Results and Discussion**

### **1. Concept of CRF and SRF and their R&D history**

Although there is no clearly distinguish between CRF and SRF in literature and the same fertilizer could be defined as SRF or CRF (UNIDO& IFDC, 1998), it is necessary to classify the two fertilizers because they are manufactured by different materials and techniques with different properties. Authors of the paper agree with Oertli (1980) , Goertz (1993a) and Shaviv (2005) and call for distinguishing CRF from SRF because the technology to manufacture CRF is more advanced now in order to ensure the quality of CRF and SRF. T separate the two fertilizers will be benefit to enterprises both of CRF and SRF manufacturers.

CRF is defined as high polymer coated fertilizer and its nutrients release is controlled by temperature and coating thickness only. Longevity of a CRF is fixed after its production. The longevity of CRF increases with coating thickness and decreased with temperature. Only coating method is able to modify pattern of nutrients release and high polymer and a fixed coating thickness control nutrients release (Goertz, 1993b). SRF is either modified N fertilizer or one its N available period is significantly longer in the soil by addition N inhibitors to N fertilizers (Amberger, 1989; McCarty, 1990). The N availability of SRF is affected by a lot of factors such as soil water content, temperature, pH, aeration, Eh,

microorganisms, texture et al. When the conditions are favorable to N conversion, for example urea hydrolyzation and nitrification, period of N validity of the SRF will be shortened.

Since start of SRF research in China in 1960's, the history of research on CRF in China comprises three stages: 1) the exploration period from 1960 to the 9<sup>th</sup> five year plan (1991 to 1996); 2) the popularization period from 1997 to 2005; and 3) the integration period with industrial production of CRFs from 2006 to now. During the 1<sup>st</sup> stage great effort concentrated on slow release N fertilizer (Feng, 1995; Xie, 1996; Zhu, 2003). During the 2<sup>nd</sup> stage, scientists in south China agriculture university (SCAU) and the other organizations have engaged in CRF studies. Following 7 aspects are recognized as achievements. 1) Nutrients release mechanism, release pattern and evaluation of the release rate have been thoroughly studied (Fan et al., 2001, 2005, 2009; Zheng et al., 2001); 2) Coating materials such as solvent based polymer (SBP), solvent free resin (SFR), and water medium resin (WMR). SBP is a popular coating material applied in most CRF companies now. However, its main problem is that the solvent cannot be recovered 100% and even less solvent lost will result in the air pollution. That is why SFR, plant oil as main coating material, has been developed and applied in CRF manufacture. The coating layer formed through reaction of two to three kinds of coating materials on surface of substrate fertilizer granular. The WMR is also environment friend coating material. The corresponding coating technique of SFR and WMR have been studied and developed in South China Agriculture University (Fan, et al., 2009). 3) Application and effects of CRF on crops has been proved (Zheng et al., 2001; Yin et al., 2006; Tang et al., 2006; Zhu et al., 2003; Li et al., 2007; Zhang et al., 2002; Li et al., 2005; Fang et al., 2004; Shi et al., 2005; Zhang et al., 2004, 2006; Zhu et al., 2000; Wang et al., 2002, 2006; Yu et al., 2003; Sun et al., 2006). 4) Fast method to predict longevity and to control quality of the CRF has been established (Dai et al., 2006, 2007). 5) Technique and method to manufacture fluid bed coating machine and coating drum have been developed in China (Fan et al., 2009). 6) Varieties of laboratory and pilot scale products of coated compound (CRF) and PCU as well as buck blend cooperated with PCU or CRF (controlled BB fertilizer) are recognized as a new measure to promote nutrient management stratagem to field crop. 7) By the end of the 2<sup>nd</sup> stage some technologies were applied by several CRF companies to establish CRF production line and to produce coated CRF. In the 3<sup>rd</sup> stage fertilizer a lot of technologies and techniques have been integrated with industrial production of CRFs to realize CRF industry over China. They are Sanyuan Planta CRF company, Shikefeng Chemistry Industry Co., LTD. and Shandong Kingenta Ecological Enginnering Co., Tld to produce CRF emerged in China.

## 2. Dynamics and thermodynamics of N release from CRF

Three domestic CRFs (PlantA) made by SanYuan Planta CRF company were studied and by taking Scotts CRF as control. Results implied that *Parabolics diffusion law*, *First order equation* and *Zero order equation* were similar to describe N release of CRFs. However, beside Scotts 150 d treatment the *r* value of Parabolics diffusion law was the maximum with a small *SE* for PlantA CRFs at both 25□ and 40□. Therefore, *parabolics diffusion law* was suggested and selected as dynamic equation to characterize N release of CRFs in routine research for convenience.

The results showed that velocity constant (*k*), being average release rate (percentage per hour), increased significantly with decrease of longevity. The calculated constant (*k*) (0.0039, 0.0064, 0.0088) was no significant difference from measured one of each CRFs being 0.0037, 0.0058, 0.0081 at 25°C. The results implied that *Parabolics Diffusion Law* is suitable to describe N release from CRF quantitatively under normal temperature condition (Fan and Yu, 2005).

Results of thermodynamic properties of nitrogen release of CRFs indicated that N release requires energy for fast nutrient supply. The apparent activity energy (AAE) of N release from four CRFs was in the same order of PlantA 300d > PlantA 240d > PlantA 180d > Scotts 150d by use of *Parabolic diffusion law*, *Elovich equation* and *Zero order equation*. The results imply that when the longevity is doubled and the AAE of N release doubled as well. In other word release of N from CRF with a longer longevity, such as PlantA 300d, requires much more energy, which explains why N supply of CRFs with longer longevity can last for a long period and why N supply is fast at higher temperature. It could be concluded that the more the longevity of CRF, the more energy and longer time consumption to release nutrient of the controlled release fertilizer (Fan and Yu, 2005).

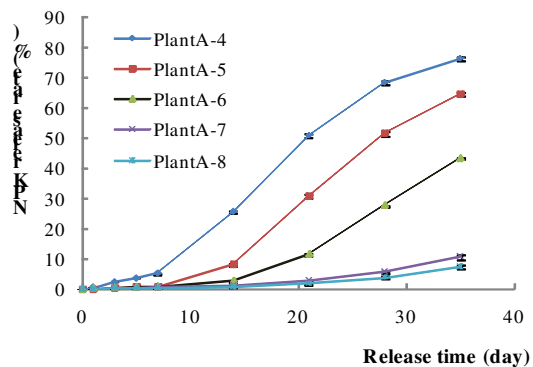


Fig 1. Effect of coating thickness on total NPK release at 25°C in stable pure water cultivation

### 3. Effect of coating film and its structure on nutrients release

In addition to energy, coating film thickness and structure influence nutrients release as well.

Fig 1 shows the effect of 5 thickness, being 4%, 5%, 6%, 7% and 8% of coating materials of substrate, on NPK release rate. From figure 1 it could be concluded that the more the thickness the longer the release time. The reason of the coating thickness effect on NPK release is shown in figure 2. The coating material covered the substrate (fig 2 on left) and there were clear sub-layers which is the pathway of nutrient through the coating film. On the surface of the coating there was also a lot of micro-pores (fig 2 on the right) which is the channel for water and nutrients passing. From figure 2 on the left it is easily understood that the pass way cross the film will be more complex if the coating thickness increased. This explains why the more the thickness of the film, the slower the release rate.

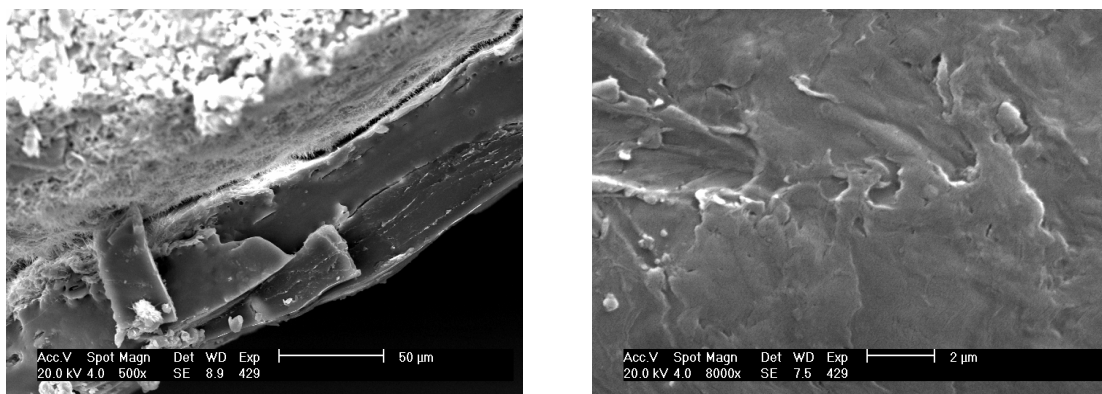


Fig 2. Photos of coating layer section and coating film surface by scanning electric microscope (SEM)

### 4. Effect of coating technique parameters on manufacturing of CRF

Nutrients release is depended on coating quality. The coating quality is influenced by coating agent, amount of substances, ratio of two main class coating materials (CoatM). The effect of each of the three parameters on coating quality could be evaluated by initial release rate (IRR) and differential release rate (DRR) (Dai and Fan et al., 2006) under 25°C. The IRR is the nutrients release rate from coated fertilizer

within 24h incubation. The DRR is release rate within 7 days subtracting the first day's rate and divided by 6. Results showed that with the increase of coating CA both IRR and DRR decrease significantly. The optimum amount of CA is 8% of the total CM in this study (Fan, Zheng and Liao, unpublished data).

Substrate magnitude (SM) affects every once application amount of CM and time of coating and then influence the coating quality. Results showed that under the same amount of CM, both IRR and DRR reduced with the increase of substrate magnitude. When the amount of substrate reaches to 10 kg per batch for urea and 12 kg for compounds, the coating quality is perfect by use of laboratory scale batch process fluid bed. Research indicated that when the CoatM 1 consumed is equal to CoatM 2 the initial release rate is small. It could be concluded that when the ratio of CoatM 1 to CoatM 2 near to 1, coating quality is the best (Fan, Zheng and Liao, unpublished data).

From the discussion above it can be concluded that the coating agent magnitude, amount of substances and ratio of coat material influence coating quality greatly. The optimum coating agent magnitude is 8% of total coating. The substrate should be enough for coating and the optimum amount for one batch of laboratory fluid bed is 10 kg of urea or 12 kg of compounds. The two coating materials should be supplied at the same amount during coating to produce high quality CRF.

## **Outlook of CRF research and development in China**

### **1. Disparities existing in field of CRF research and development**

Compared to advanced countries, there still exist a lot of disparities in field of CRF industry. Although Chinese scientists have paid great attention to basic research on CRF and obtained many new achievements on developing coating materials such as water medium resin (WMR) and solvent free resin (SFR), design and manufacture of coating machines such as fluid bed and coating drum, new types of CRF products development such as multiple release rate CRF and field crop CRF, the level of CRF industry is still behind the advanced nation such as USA and Canada. The CRF quality of some small companies is still not stable. The techniques of drum coating process lag behind America and Europe. Therefore, the future direction of CRF R&D in China is to tackle the key problems in CRF research and industry by incorporation all aspects researchers and their achievements to focus on promoting CRF technology into industry and improve quality of CRF products.

### **2. Field of CRF research and development in future in China**

In view point of requirement, the following fields in controlled release fertilizer research should be considered in future in China.

In field of controlled release technology, the technique to control release curve being a sigmoid pattern, technology to produce controlled buck blend to fit field crops needs and controlled release technology not governed by temperature should be further studied.

Technique to manufacture CRF with lower energy consumption and solvent free and surface reaction coating techniques should be promoted in large scale. Water medium resin to produce CRF should be paid great attention. Substrate fertilizer of CRF, especially its physical properties including hardness, surface property and nutrients composition must be studied which influence controlled quality greatly.

The national standard of CRF and formal method to evaluate longevity accurately and fast should be established to ensure the quality of CRF production.

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