



Dewatering of coal fines using a super absorbent polymer

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Synopsis

In most coal preparation processes, water is a necessary medium, but the presence of water in coal after it has been cleaned has a negative impact on transportation costs, handling and specific energy values. The utilization of super absorbent polymers (SAP) in the nappy application is well known. The concept of utilizing these polymers was investigated for the purposes of dewatering coal and other fines, generated by preparation processes such as flotation. SAPs are granular highly cross-linked synthetic copolymers with excellent water-absorbing properties.

The dewatering process is characterized by three main stages: (a) contact of super absorbent polymer with high-moisture fine coal; (b) separation of dewatered fine coal from super absorbent polymer; and (c) regeneration of used super absorbent polymer, by exploiting its response to changes in conditions such as pH or temperature.

Preliminary tests showed the separation step to be very difficult. The novel idea of encasing a given amount of polymer in a water permeable cloth solved this problem (of separating the swollen polymer from the dewatered coal). Preliminary tests investigating the effectiveness of the sachets of polymer showed a drastic decrease in the moisture contents of slurries.

Furthermore, it was shown that it was possible to regenerate the polymer (still within the sachets) through thermal drying. A full-scale experimental programme was then followed to accurately determine the feasibility of using sachets of SAP. The experimental variables were initial slurry moisture content and polymer dosage. It was observed that the sachets seemed to work fastest and most effectively at high moistures and also at higher dosages of SAP.

Regeneration of the polymer was also investigated, using two methods: thermal regeneration and pH-induced regeneration. The experimental variables, for investigating the regeneration process, were method of regeneration and grade of water used. Thermal regeneration at 70°C seemed to work successfully. Although the cost of using thermal energy is still a problem, the safety aspect (fire hazards) has been addressed since the polymer does not ignite when heated, unlike fine coal particles that may do so. The alternative method of regeneration, which exploits the pH-sensitivity of the polymer, was less successful, and further work needs to be conducted.

Introduction

Coal preparation is used to upgrade run-of-mine coal before it is utilized by the end-user, primarily electric utility power plants. According to Fonseca¹, the coal preparation process reduces the amount of non-

combustible mineral impurities, acid-rain precursor sulphur-bearing minerals and hazardous trace elements, and generally produces more uniform, higher energy content fuels. Most conventional and advanced coal cleaning processes, unfortunately, involve the use of water. Dewatering of the fine, clean coal to a low moisture level (<10% w/w) is often a problem. Excessive moisture in the final product is a great concern for utility companies since various handleability problems result. Current fine coal dewatering technologies include press filters, dewatering screens, thermal drying and centrifugal dewatering, and although each of these technologies has its own particular benefits, they also have drawbacks. According to Kamall² thermal drying is the only fully developed method that can currently be used to achieve low moisture content within product specification (approx. 9% w/w) after applying press filters or dewatering screens. Utilizing thermal methods is not the best option due to the safety hazards and high operational cost. Super absorbent polymers (SAPs) could provide a viable alternative, since these polymers are granular, highly cross-linked synthetic copolymers with excellent water-absorbing properties³. SAPs have been reported, by Dzinomwa⁴, to absorb water to moisture levels comparable to those resulting from thermal drying (<10%). Their ability to be regenerated by various means also makes this option highly attractive.

Experimental

According to Dzinomwa⁴, the dewatering process using SAPs consists mainly of three stages: (a) contact of fine coal with the polymer; (b) the separation of SAP from the dewatered coal, and (c) the regeneration of the

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SAP. Stage (c) can be conducted by two methods: (1) temperature-induced regeneration or (2) pH-induced regeneration.

The SAP was presented in the form of dry, granular, white beads. Each of the following steps, except the construction of the sachets, was followed as outlined by Dzinomwa⁴.

Preliminary investigations

The first step in this experiment was to visually investigate the absorptive capacity of the polymer. Approximately 1g of the dry polymer was added to 1500ml distilled water and tap water, respectively. The polymer-water mixture was not stirred, and the beakers were covered with foil to prevent evaporation. A spatula full of the polymer was also added to a coal slurry with an unknown moisture content, and observations noted. The aim of these tests was to remove the swollen polymer from the water media at regular intervals and weigh them, so as to monitor the progress of the absorption step.

Using the SAP in sachets

Separation of the swollen polymer from the dewatered coal had previously been a problem and to solve this, a novel idea was conceived. Sachets containing various amounts of polymer were constructed and placed in coal slurries of varying moisture contents (30%, 45%, and 60%). These sachets were made of 'Tidy Roll Cloth' which is a non-woven, wiper roll cloth that would allow the polymer to absorb water from a slurry without direct contact with the coal. The buckets containing the slurries were covered to prevent evaporation, which could lead to unreliable results.

Stage (a) of the dewatering process was investigated and was conducted by following four main steps:

- ▶ A passive contacting period between the polymer and the slurry (~22 hours)
- ▶ A mixing stage (2 hours)
- ▶ A further four hours of passive contact between the slurry and the polymer
- ▶ A final 48 hours of passive contact.

The process was also investigated using 10% polymer dosage and mixing for a period of 25½ hours followed by a passive contact period, between the polymer and the coal, for a further 53½ hours. This was compared to results obtained when using the same polymer dosage (10%) but without any mixing i.e.: passive contact for 79 hours.

Regeneration of super absorbent polymer

According to Dzinomwa⁴, regeneration of super absorbent polymers could be done following either one of two processes: temperature-induced regeneration or pH-induced regeneration.

Temperature-induced regeneration

Four sachets, each containing 1g of dry SAP granules, were prepared. Two of the four sachets were allowed to absorb distilled water and the other two, tap water (at room temperature). The swollen sachets were dried at 70°C for ~24 hours, resulting in re-usable sachets. The above procedure was repeated using the same four sachets for seven cycles.

pH-induced regeneration

Super absorbents are reported by Dzinomwa⁴ to be very sensitive to pH. According to Jhon, *et al.* the polymer absorbs the maximum amount of water around neutral pH and very little on either side of the pH scale. Water is released from the polymer by acid treatment; this causes the pH of the collapsed polymer to be too low for any further absorption of water. For a polymer to absorb water again it must be neutralized by treatment with a base.

Tap water and distilled water were used for experimentation. Six sachets, each containing 1g of dry SAP granules, were prepared. Approximately 100 ml of distilled water was added to three sachets and 100 ml tap water was added to the other three sachets. Approximately 10 ml of 1M HCl was added to the swollen polymers while still contained in the sachet, to lower the pH. This induced the collapse of the polymer and led to the release of the absorbed water.

Approximately 5 ml of 2M NaOH was added to the collapsed polymer contained in the sachet to neutralize the pH, change the polymer groups to a more ionised state and restore the swelling capacity. The acidic water released from the polymer was also neutralized to allow for safe disposal. A fourth step could be applied to the process, namely thermal drying, but it was not necessary to dry the polymer after neutralization for it to absorb moisture again. The above steps were repeated for four cycles using the same sachet.

Results and discussion

The results for each experiment are presented with their respective discussions.

Preliminary investigations

On addition of the dry polymer to the water, almost immediately a distinct swelling of the SAP was observed. The polymer in the distilled water appeared to absorb water at a faster rate than the polymer in the tap water. After fifteen minutes an attempt was made to remove the gel from the water for a mass measurement. However, the poor handleability of the polymer prevented this. The sample never reached a stage where it could be removed for weighing, even after several days.

On addition of the dry granules of SAP to the slurry, an immediate reduction in the moisture content was observed. The SAP particles also appeared to swell. However, it was impossible to successfully separate the swollen polymer from the dewatered coal for a mass measurement.

Using the SAP in sachets

The sachets containing SAP were quite effective in absorbing water, whether it was pure water or from the coal slurry. The cloth material of the sachets apparently did not hinder the dewatering process and allowed the scraping off of the excess dewatered coal from its surface. Thus the previous problem, of not being able to separate the polymer and weigh it in its swollen state, was overcome.

On addition of the sachets containing dry SAP granules to the slurries, a distinct swelling of the polymer in the sachets was observed. All of the slurries showed a decrease in moisture content after the 22-hour contact period (without mixing). The two hours of mixing that followed, showed a

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further decrease in moisture content. After another four hours of passive contact (without mixing), a further decrease of moisture content was observed, as was after a further 48 hours.

Graph 1 shows the effect that different polymer dosages have on slurries with 30% moisture content. The slurry containing 30% moisture was observed to lose a maximum of 76% of its moisture after the complete cycle, when using a 2.0% polymer dosage. The curve of the graph shows that at all the higher polymer dosages, the moisture content initially decreases sharply (step 1) as observed by Dzinomwa⁴ and this is then followed by a further decrease in moisture once mixing of the slurry (step 2) is carried out. The lower polymer dosage (0.5%) does not show such a sharp decrease.

Thus, the report by Dzinomwa⁴ that polymer dosage plays an important role in the effectiveness of the dewatering process has been verified here. The decrease in moisture content by 0.5% dosage is comparable to that by 1.0% dosage at step 2, but thereafter it is clearly shown that the higher dosage is much more effective. It is also similarly confirmed that mixing of the slurry with the polymer is crucial, as observed by Dzinomwa.

Graph 2 shows the effect that different polymer dosages have on slurries with 45% moisture content. The slurry containing 45% moisture was observed to lose a maximum of 80% of its moisture after the complete cycle, when using 1.0% polymer dosage. Here the same sharp decrease seen in Graph 1 is observed. The mixing step (step 2) is observed to consistently cause a further decrease in the moisture level of the slurries. However, on standing, the moisture content increases once again (step 3). This implies that mixing in slurries with high initial moisture content causes the water to be released from the polymer and then re-absorbed on standing.

Graph 3 shows the effect that different polymer dosages have on slurries with 60% moisture content. The slurry containing 60% moisture was observed to lose a maximum of

88% of its moisture after the complete cycle, when using a 2.0% polymer dosage. The high initial moisture content has enhanced the results. For all three polymer dosages the same sharp decrease in moisture after step 1, seen in Graph 1 and Graph 2, is observed.

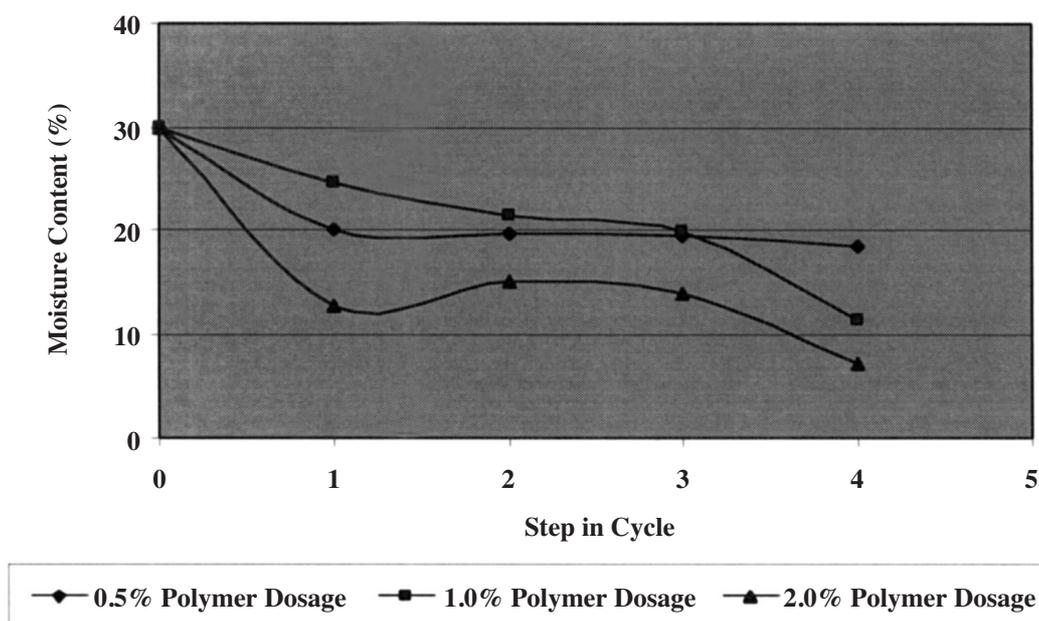
A polymer dosage of 0.5% showed a high increase in moisture after mixing (step 2), implying that the absorbed water was released extensively. Thereafter the moisture decreased gradually on standing (steps 3–4).

The polymer dosage of 1.0% also showed an increase in moisture content on mixing, albeit to a lesser degree. Thereafter the moisture content decreased and showed a tendency to level out at the end of the cycle.

The polymer dosage of 2.0% did not show such a drastic increase in moisture content on mixing. It is assumed that the high dosage of the polymer was sufficient to hold the absorbed water—preventing its release during mixing. The moisture content continued to decrease on standing (steps 3–4).

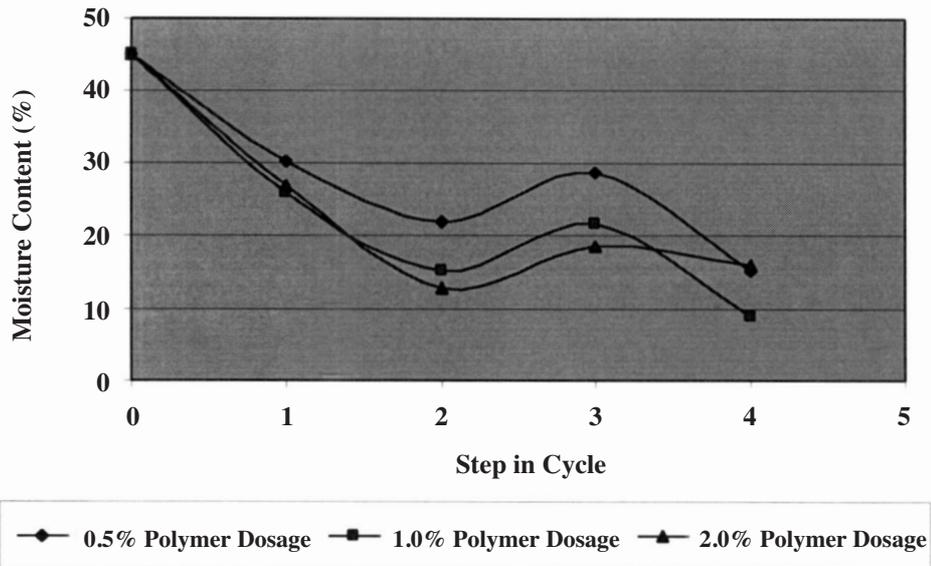
Graph 4 shows how the slurries react to a 10% polymer dosage with mixing for 25½ hours followed by 53½ hours passive contact. The mixing step has reduced the dewatering of the 30% and 45% moisture slurries, and the passive contact period shows no significant further decrease. However, for the 60% slurry the moisture decreases quite drastically and, after it has been mixed for ~7hrs, starts to increase again. Once the mixing period of 25½ hours is completed the water is not re-absorbed on standing as observed previously (Graph 3). This implies that mixing for more than 7 hours results in an irreversible breakdown of the interaction between the polymer and the absorbed water.

Graph 5 shows how the slurries react to a 10% polymer dosage without any mixing i.e.: 79 hours passive contact. It can be seen that the moisture contents are reduced at a very slow rate. The final moisture contents are also not as low as when the slurries are mixed.

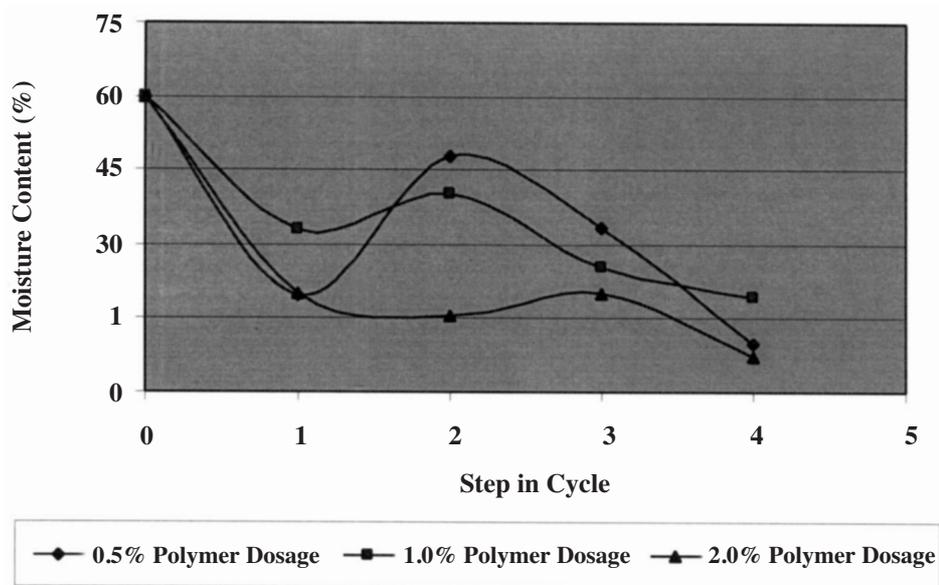


Graph 1—Effect of polymer dosage on moisture content (30% initial moisture content)

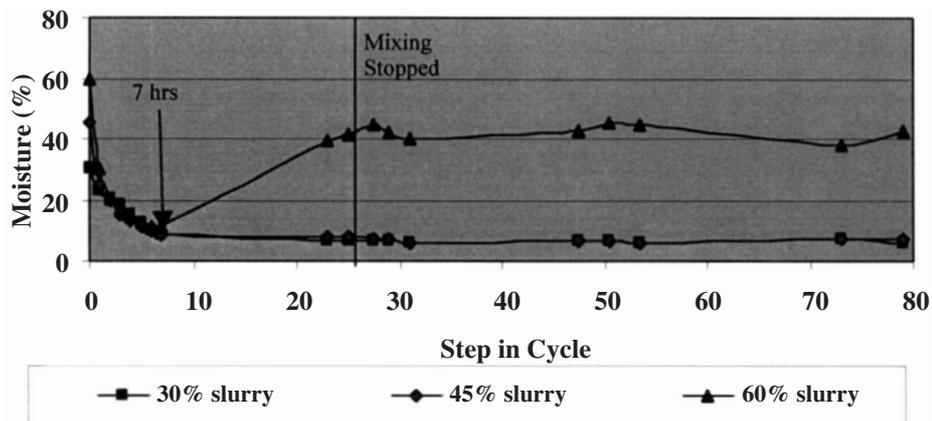
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Graph 2—Effect of polymer dosage on moisture content (45% initial moisture content)



Graph 3—Effect of polymer dosage on moisture content (60% initial moisture content)



Graph 4—Effect of mixing on moisture content with 10% polymer dosage

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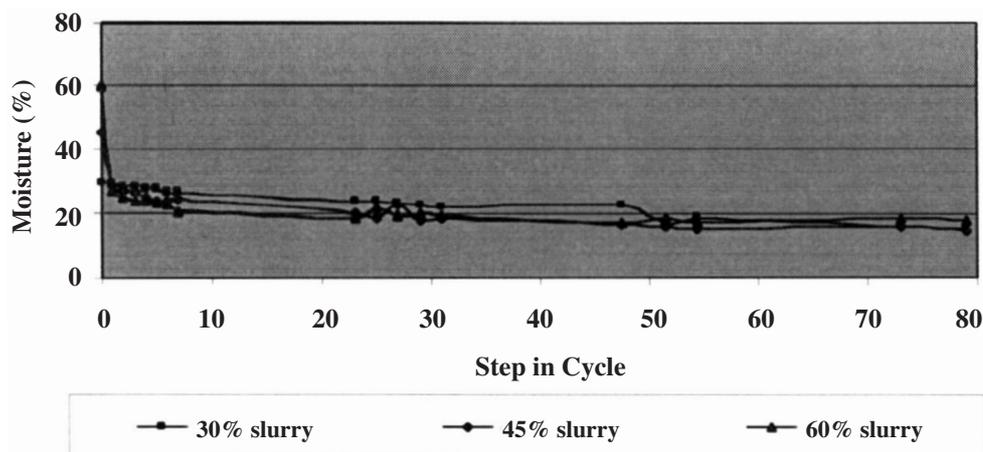


Figure 5—Effect of not mixing on moisture content with 10% polymer dosage

The summary of results is shown in Table I. On the whole, the polymer performed best at high initial slurry moisture contents and 2.0% polymer dosage. The maximum reductions in moisture content are shown in bold. Final moisture contents are also shown in the Table.

Regeneration of super absorbent polymer

Temperature-induced regeneration

Table II shows the absorptive capabilities of the polymer as well as the changes in mass, as the sachets containing SAP are regenerated through thermal drying.

The polymer was able to absorb ~90 times its own mass of water. Observing the shaded areas of Table II, it can be seen that the SAP within the sachets absorbed approximately 95% of the 100 ml distilled water added, and for the sachets treated with tap water, the SAP absorbed about 85% of the water added. As observed by Dzinomwa⁴, drying the sachets at 70°C removed most of the absorbed water and resulted in sachets with dry and clustered SAP granules. These sachets were able to again absorb considerable amounts of water, implying that they can be thermally regenerated and used several times. Hence, instead of thermally drying fine coal, the polymer absorbs the moisture from the coal and the polymer is instead thermally dried. This implies safer practices, since heating fine coal sometimes leads to it igniting², whereas the polymer dries quite safely.

pH-induced regeneration

As shown in Table III, the sachets containing SAP absorbed ~100 ml of distilled water in the first cycle and those that were treated with tap water absorbed ~80 ml of tap water. The difference is probably due to the presence of dissolved ions⁴. When HCl was added to the sachets that were saturated with water, 80% of the absorbed distilled water was released, and about 90% of the absorbed tap water was released. The reason for the difference in water release may be due to tap water containing minerals that may also influence the pH of the water². For the SAP to absorb moisture optimally, the pH has to be at neutral⁴. After neutralization with sodium hydroxide, the volume of the released water was slightly decreased. It may have been that

the polymer had re-absorbed some of the released water immediately after neutralization.

The 'regenerated' polymer absorbed only about 30 ml of water in the second cycle and even less was released. The absorptive capability of the sachets continued to decrease for cycle 4 and cycle 5. Hence, the cycles of regeneration were very few, when compared to thermal regeneration. It can also be seen that the tap water allowed the polymer to go through only three cycles, indicating that the presence of dissolved ions were again affecting the absorption process.

Conclusions

According to the preliminary investigations into the use of SAP as a dewatering agent, separation of the swollen polymer from the dewatered coal proved to be very difficult. It did not allow for mass measurements and was not practical when considering the implications in the commercialization of SAP as a coal-dewatering agent.

Using a water-permeable cloth as a barrier between the slurry and the polymer was a novel idea that solved the problem of separation. The sachets of polymer that were constructed were able to effectively draw water out of the medium and swell several times in size. An experimental programme was constructed and involved variables of polymer dosage and initial slurry moisture contents. The laboratory experiments conducted over a period of ~76 hours on slurry mixtures, with phases of mixing, showed that it is possible to decrease moisture contents by ~70% (on average) using SAPs. A final moisture content of ~13% (on average) was obtained. It was observed that the sachets seemed to work fastest and most effectively at high moisture contents and also at 2.0% dosages of SAP.

Using a 10% polymer dosage and mixing for long periods of time (more than 7 hours) adversely and irreversibly affects the interactions between the absorbed water and the polymer when dewatering a slurry of 60% moisture content. For the 30% and 45% slurries, mixing helps in reducing the moisture content, although mixing for more than 7 hours does not show a significant further decrease. It can therefore be concluded that mixing for 7 hours is the maximum time period necessary.

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Table I

Summary of results

Polymer dosage	Initial moisture (%)	Final moisture (%)	Loss in moisture (%)
0.5%	30	18.32	38.93
1.0%	30	11.38	62.07
2.0%	30	7.18	76.07
0.5%	45	15.08	66.49
1.0%	45	8.88	80.27
2.0%	45	15.98	64.49
0.5%	60	9.78	83.70
1.0%	60	19.36	67.73
2.0%	60	7.18	88.03
Averages		12.57	69.75
10.0% (mixing)	30	5.96	80.13
10.0% (no mixing)	30	15.21	49.30
10.0% (mixing)	45	7.00	84.44
10.0% (no mixing)	45	14.95	66.78
10.0% (mixing)	60	42.41	29.32
10.0% (no mixing)	60	17.95	70.08
Averages		17.25	63.34

Table II

Results from the temperature-induced regeneration experiments

Grade of water	Cycle 1		Cycle 2	
	Dry mass of sachets (g)	Volume of water absorbed (ml)	Dry mass of sachets (g)	Volume of water absorbed (ml)
Distilled	2.48	94.30	14.55	87.00
Tap	2.47	84.75	7.85	79.75
Grade of water	Cycle 3		Cycle 4	
	Dry mass of sachets (g)	Volume of water absorbed (ml)	Dry mass of sachets (g)	Volume of water absorbed (ml)
Distilled	2.62	90.75	2.40	85.75
Tap	2.64	70.75	2.44	81.25
Grade of water	Cycle 5		Cycle 6	
	Dry mass of sachets (g)	Volume of water absorbed (ml)	Dry mass of sachets (g)	Volume of water absorbed (ml)
Distilled	3.75	99.50	3.37	99.50
Tap	2.87	91.40	2.58	93.90
Grade of water	Cycle 7			
	Dry mass of sachets (g)	Volume of water absorbed (ml)		
Distilled	3.09	92.50		
Tap	5.74	85.50		

Table III

Steps involved in pH-induced regeneration

Cycle	Grade of water	Distilled pH 6.6-7.0	Tap pH 7.3-8.0
1	Volume of water absorbed (ml)	100	86
	Volume of water released (ml)	81	76
2	Volume of water absorbed (ml)	36	25
	Volume of water released (ml)	35	19
3	Volume of water absorbed (ml)	15	4
	Volume of water released (ml)	11	3
4	Volume of water absorbed (ml)	2	0
	Volume of water released (ml)	4*	0

* Not reliable results

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The fact that higher polymer dosages are more effective has financial implications in terms of the amount of SAP needed to dewater a given amount of coal, as well as time constraints. However, more vigorous experimentation could prove the dewatering of fine coal by SAP to be economically feasible.

Regeneration of the polymer was also investigated. Thermal regeneration was more successful than the pH-induced regeneration. Coal is thermally dewatered at temperatures in excess of 50°C. Thermal regeneration of the polymer is not economically feasible since heat energy is still required. However, in terms of safety requirements, thermal regeneration is more advantageous since the polymer does not ignite at elevated temperatures, as experienced when thermally drying fine coal. The 'regenerated' polymer was not able to absorb as much water as the original granules, but this was possibly due to errors in the neutralization step of the regeneration. Hence, it may still be possible, if correctly conducted, to regenerate the polymer using the pH-dependent technique. Further research may still need to be implemented regarding the regeneration of the SAP.

Note: The experiments were done in a laboratory environment and improvements need to be explored for practical reasons, while still maintaining the idea of sachets containing SAP.

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IsoMetrix, new web-based SHEQ Software launched*

Metrix Software Solutions announced the release of IsoMetrix, new web-based software for the management of environmental, quality, health and safety management systems. IsoMetrix has been developed through the collaborative efforts of Metago Environmental Engineers (Pty) Ltd, a leading environmental engineering consultancy and ASYST International, an international software development house.

Isometrix is a latest generation product and is based upon the success of Metago's safety, health and environment management (SHE) system. The tools have been designed around user requirements to assist organizations in obtaining and maintaining their management systems and also their ISO 14001 certification. The software has been used with great success at a number of the world's largest mining and utility companies. Existing clients include such household names as Anglo Coal, Anglo Platinum, De Beers, Eskom and Impala Platinum.

'This is a case where the combined efforts of experts in their respective fields have yielded a product that not only provides exceptional functionality as a SHEQ management tool, but is now also built using the latest web development and programming practices, resulting in stable, flexible software,' commented Paul De Kock, Director of Metago. 'The software dramatically improves an organization's ability to manage corporate risks effectively and to achieve certification to international standards such as ISO 14001 and OHSAS 18000.'

'Where Metago is a well-established, professional engineering and environmental management consulting company,' added Paul Marketos, MD of ASYST International, 'ASYST International is a reputable software house that specializes in the development of thin client applications. We have taken Metago's tried and tested existing management system and redesigned it as a web application. IsoMetrix therefore not only has the core functionality and exceptional design that has made it the leading SHE management tool in SA, but it also now has technical advantages such as increased stability, speed and performance, improved analytical and reporting capabilities and rapid, flexible and cost-effective deployment. This takes the system to a new level that exceeds global standards.'

'World pressure is demanding that companies monitor and manage environmental, quality and social risks,' continued Dennis Marketos, Chairman of Metrix Software Solutions. 'This is the first phase of developing a single software product that will meet the needs of safety, health, environment, quality and risk users. We are delighted to be able to offer our clients quality software coupled with expert advice.'

The Quality module of IsoMetrix will be released later in the year. ◆

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Chinese crude steel production fuels rapid rise in manganese output

New report analyses global manganese supply and demand

A new report from market analyst Roskill says that world production of contained manganese reached 7.6 Mt in 2001 and remained around that level in 2002, marking a strong recovery from the late 1990s when output was hit by a slump in the global steel industry. The *Economics of Manganese* (10th edition, 2003) says that world output is soon set to match the 1996 peak of 8.2 Mt, a level not seen since the 1980s prior to the break-up of the Soviet Union and the collapse of much of its huge manganese industry.

The report says that much of the growth in output is being driven by the relentless increase in Chinese production of crude steel, by far the largest in the world, which continues to expand at rates not seen elsewhere. Roskill says that analysis of trends in terms of contained manganese provides a better overall picture than is obtained from gross output, because China, which has the world's largest mine output, produces mainly low-grade ore and its large annual fluctuations in production tend to obscure the global pattern. Over the last decade or so, the world trend in supply of contained manganese has been fairly flat or increasing only slightly.

Fewer countries producing manganese ferroalloys

The report says that world production of manganese ferroalloys (ferromanganese and ferrosilicomanganese) was more than 7 Mt in 2000 and 2001, a level rarely matched during the 1990s. Production in 2002 was probably around 5% higher, the result of a large increase in steel output in China. In recent years South Africa, China and the Ukraine have together accounted for 50-60% of world production of manganese ferroalloys. Roskill says that the predominance of these countries, large year-on-year fluctuations in output and the fact that their production is on a generally upward trend, tend to obscure the major changes that have taken place in the industry. There are now fewer countries producing manganese ferroalloys than there were a decade ago: some major producers, like the UK and Canada, ceased production in the early 1990s, while others, such as Germany and Japan, have greatly reduced their output. Nevertheless, the industry remains broad based in geographical terms.

Overcapacity cuts forecast

In 2001 the manganese ferroalloys industry had an estimated overcapacity of some 40%, much of it is located in

China and the CIS. Roskill expects that this should be cut significantly by 2004. Much of the reduction will come from the closure of some of China's 800 operations, fewer than 10 of which are thought to be profitable.

Other cuts may come from India, where producers are struggling with escalating power costs, the removal of import duties and the imposition of anti-dumping duties by the USA.

It is highly likely that the manganese industry will see further concentration of ownership as the privatization process progresses in China and India, and the CIS and the major corporate groups continue with a strategy of integrating worldwide mining and smelting operations. In the CIS, foreign investment is seen as crucial to the restructuring and rehabilitation of the manganese industry.

No new large-volume markets in sight

Around 95% of manganese output is consumed in metallurgical applications, mainly (90%) in the steel industry. With no new large-volume markets for manganese on the horizon, demand will continue to reflect the trend in world steel production, which, while cyclical, is on a long-term upward path. Steel production in the early part of the 21st century is at a record level and consumption is forecast to increase by over 10% between 2002 and 2007. In the short to medium term, the phasing out of obsolete steel-making plants in many parts of the less developed and developing world may impact on manganese usage as unit consumption falls in line with increasing production efficiencies. In the longer term, this will be more than offset by greater demand resulting from overall growth in steel production.

Rapid growth in battery market

Manganese has a wide range of non-metallurgical end-uses, by far the largest of which is the production of primary and secondary batteries. Over 250 000 tpy of electrolytic manganese dioxide are consumed by the battery industry, and demand is growing at 4% to 6% pa. However, manganese faces some competition in this end-use from other types of battery and from non-battery power sources. *The Economics of Manganese* (10th edition 2003) is available at £1500/US\$3000 €625 from Roskill Information Services Ltd, 27a Leopold Road, London SW19 7BB, England. Tel: +44 20 8944 0066. Fax: +44 20 8947 9568. E-mail: info@roskill.co.uk ◆