Number 455

July | August 2013

INTERNATIONAL Fertilizer

Tea's nutrient needs

SYMPHOS 2013: innovation at the forefront

FSU potash investments gather pace

Maximising water use efficiencies

We assess advances in the technology to minimise water consumption and losses throughout the phosphate and potash mining and manufacturing processes.

The Ostara process promises the opportunity to treat and discharge or reuse excess pond water volumes on a continuous basis.

Water is an essential part of mining and processing operations in both the phosphate and potash sectors, being essential for the processing of the mineral ores, dust control, irrigation, the cooling of machinery and staff amenities. Minerals processing tends to use the most water within a mining operation. (*Water Use in the New South Wales Minerals Industry*, NSW Minerals Council.)

Mines can use a large proportion of the available water in a region, particularly in phosphate operations conducted in the semi-arid regions of the Middle East. Companies tend to view water strategically and are driven to use water efficiently due to its low availability in some areas and the need to ensure continuing operations, the expectations of the community and the cost of using water.

Mines get their water from a variety of sources, depending on local conditions and requirements. Sources include rivers, groundwater aquifers, rainfall, water recycled on site, local authority fresh water supply or water supplied by a third party, including other mines. While water quality is important for some aspects of mining and minerals processing, lower quality water such as treated effluent and saline groundwater can be used for some purposes. This reduces a mine's demand for higher quality water, which can have environmental benefits as well as leaving higher quality water for others in the community. Mines frequently have water treatment facilities on site, so that lower quality water can be treated to a quality that is "fit-for-purpose" – that is, treated to a quality that is suitable for the purpose being used. Most phosphate and potash mines now recycle a high proportion of their water on site, with some mines recycling up to 90% of their water.

Because water is so critical for mining and downstream operations, phosphate and potash companies now implement sophisticated water management plans which can include significant data collection and water monitoring and analysis, providing an accurate picture of the quantity and quality of available water and water needs. This is particularly important when available water is low or can fluctuate widely.

Water programmes for P and K

Many phosphate and potash fertilizer producers have turned to specialist water management companies as they devise programmes to increase the efficiency of their water usage. One such company is Veolia Water, a division of the French company Veolia Environnement and the world's largest supplier of water services. Veolia Water operates in 66 countries around the world and employs over 95,000 staff. Its core activities include the provision of drinking water, waste water treatment and the production of water for industrial processes, providing treatment, heating, cooling and cleaning applications for industry.

Veolia has built 15% of the world's desalination capacity, offering two main technologies: reverse osmosis and thermal desalination. With reverse osmosis, water is passed through membranes under pressure: the membrane allows water to circulate but captures the salts. During thermal desalination, water is vaporised in distillation chambers to separate out the salts it contains.

Veolia works on reducing the environmental impact of water use through a number of strategies:

- Saving water: reducing leaks in the system and managing consumption through systems such as water meters.
- Protecting water resources: treating wastewater and preventing pollution,

for example by avoiding discharge into aquifers.
- Limiting the environmental impact of water use,
- Recycling treated water, recharging aquifers and desalinating seawater.

The Veolia Water Solutions & Technologies division has developed evaporation and crystallisation systems for many mining applications. Veolia's *HPD*® evaporation and crystallisation technology is often a critical process component in evaporates mining, by-product recovery and international process water management in the potash sector. Veolia has over 800 installations in more than 30 countries with evaporation and crystallisation systems providing critical industrial processes that:
- Produce pure products from natural deposits
- Recover by-products from waste streams
- Concentrate dilute streams
- Reduce water volumes and increase water recovery for environmental benefits.

As applied in the fertilizer sector, Veolia Water's *HPD*® crystallisation technology enables the recovery of potassium from mineral deposits in Saskatchewan, the Atacama Desert of Chile and the mineral-rich Dead Sea. The technology is also employed in the phosphates sector.

One such installation is at the Dead Sea Works (DSW) facility in Sdom, Israel. The design requirement was for a minimum nameplate capacity of 153 t/h of KCl crystals, with a consistent crystal size and purity of greater than 98% KCl, representing an increase of almost 30% in potash production capacity. The original plan was to utilise a four-stage train in the expansion, but this was later revised to a five-stage train, using Veolia's *PIC*™ draft tube baffle and *HPD*® crystallisation technology. The design provided efficient heat recovery and made sizable savings in energy consumption.

As part of the DSW expansion project, Veolia also provided all major equipment to support the crystallisation plant, including hot wells, feed tank, pumps and a custom agitator design for all five stages.

Greenfield projects

Veolia Water has been commissioned to provide water management facilities and services in two greenfield potash projects. On 21 March 2013, the company signed a contract with K+S Potash Canada GP to provide the detailed and basic engineering for the new potash production plant at the Legacy facility being developed in Saskatchewan. Veolia Water will supply the *HPD* evaporation and crystallisation technologies that will form the basis of the production of 3 million t/a of potash by 2023. The *HPD* technology will be used to recover the potassium salts contained in the deposits extracted by solution mining at the site. The facility is scheduled to begin its first potash production at the end of 2015.

On 24 May 2013, Veolia Water announced that it had completed a process evaluation for Verde Potash to support the development of its Cerrado Verde project in Minas Gerais, Brazil for the production of KCl fertilizer. Verde Potash intends to use *HPD* evaporation and crystallisation technology for the purification and production of chemical-grade fertilizer potash at the mine site.

Improved boiler water performance

PotashCorp, operator of the Aurora phosphate mine in North Carolina, USA, commissioned Veolia to tackle problems arising from boiler feed water that was high in silica and other contaminants. Mine officials decided to upgrade the boiler feed water pre-treatment system to a state-of-the-art reverse osmosis (RO) membrane system. The new system was inaugurated in March 2009 and has significantly improved operating performance, with reduced water consumption and overall operating expenditures.

The new boiler feed water pre-treatment system at Aurora includes multimedia filtration (MMF), ion exchange softening and reverse osmosis. The RO system has been designed to operate as both a single- and double-pass system. All four RO units have a 16:8 array and 144 membranes. A unique aspect of the RO system is that one of the RO units can operate in both first pass mode to produce boiler feed water and in second pass mode to supply higher purity process water.

As a general rule, PotashCorp operates the Aurora unit as a two-stage RO, in which two RO systems run in series with the permeate of the first acting as the feed to the second. For the Aurora plant, a two-stage RO is justified because the additional expenses of operating the second RO system are lower than alternative forms of polishing the first two-stage RO permeate to reach a higher quality of final product water.

The Aurora RO system consistently provides high-quality feed water, thereby ensuring greater reliability of the plant's boilers and high-purity process systems. The technology also provides PotashCorp's Aurora water treatment operators an easier system to operate, with reduced maintenance demands at the plant and lower boiler feed water costs.

Turning tailings water into process water

Veolia Water has developed the *ACTIFLO*® system, comprising a high-rate water clarification process in which water is flocculated with microsand and polymer in a draft tube. The technology is widely employed for municipal and industrial water and wastewater treatment, and it also allows tailings water to be converted into process water. One recent application of this technology has been by Barrack Gold Corporation, which operates a mine in north west Ontario, Canada. The mill at the Hemlo site requires a lot of water because its processes are in slurry form and water is continuously sent out to a tailing pond along with the tails. The tailings pond water is subsequently diverted to the polishing side of the pond for reclamation and subsequent use at the mill. Approximately 20% of the reclaimed tailings water is now redirected to the *ACTIFLO* process for clarification and metals removal.

Downstream requirements

Phosphate mining operations throughout the world are increasingly integrated with downstream production. The wet process manufacture of phosphoric acid as practised in Central Florida and many other parts of the world requires a large volume of process water that is used as a water source for the phosphoric acid, for gas scrubbing, to slurry the phosphogypsum produced and transport it to storage, to operate barometric condensers, and for a multitude of other uses in the chemical complex. (Source: Florida Industrial and Phosphate Research Institute.)

A major portion of the heat released in the phosphoric acid production process ends up in the process water and is lost to the atmosphere by evaporative cooling. The process water is stored in ponds maintained on top of the phosphogypsum stack and in a below-ground cooling pond. These ponds provide the large surface

Table 1: **Typical pond water analysis, Central Florida**

Parameter	Untreated process water
Lab pH	2.1
Calcium (mg/l)	538
Magnesium (mg/l)	223
Sodium (mg/l)	2,260
Potassium (mg/l)	210
Iron (mg/l)	59
Manganese (mg/l)	15
Chloride (mg/l)	140
Fluoride (mg/l)	4,120
Sulphate (SO_4) (mg/l)	6,200
Total phosphorus (P) (mg/l)	6,600
Ammonia N (mg/l)	1,240
Solids, total dissolved (mg/l)	39,800
Solids, total suspended (mg/l)	22

Source: FIPR

area needed for evaporation and the cooling of the water.

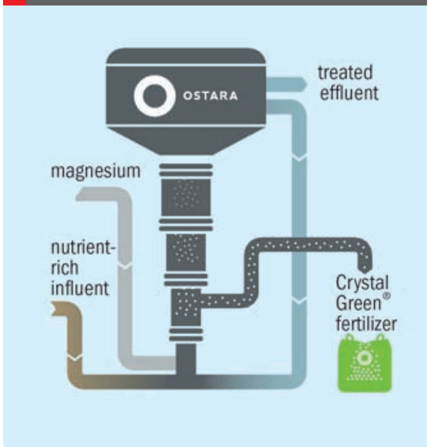
In the eyes of the phosphate producers, pond water inventories can represent an increasingly significant liability. They also draw the attention of environmental regulators. The pond water requires very careful management. For example, if one of the operating plants is shut down and it is necessary to close the phosphogypsum stack and pond water system, the water in the inventory must be treated before it can be discharged. The volume of the water to be treated could be as much as 2-5 billion gallons. The process water has a low pH of about 1-2 and contains a mixture of phosphoric, sulphuric and fluosilicic acids. It is saturated with calcium sulphate and contains numerous other ions found in the phosphate rock used as raw material as well as ammonia from the solid fertilizer manufacturing process. Table 1 shows a typical pond water analysis.

The high concentration of dissolved solids in pond water and phosphate plant process water presents a range of technical and economic challenges for treatment to ever more stringent environmental discharge standards. This relatively complex mixture tends to form various precipitates, gels and crystals which must be managed carefully to allow efficient treatment and to recover selected components in pure forms. (*Merging Cost-Effective Treatment with High Water Quality through Resource Recovery*, Ahren Britton, Don Clark and Ram Prasad, Ostara Nutrient Recovery Technologies Inc. Paper presented at AIChE Clearwater Meeting [June 2012].)

A fertilizer bonus from pond water

Ostara Nutrient Recovery Technologies is addressing these issues and has devised technology to treat and discharge accumulated pond water volumes. Ostara's goal is to develop a treatment process that economically produces a high-quality treated effluent while recovering a significant fraction of the ammonia and phosphate value in the form of a struvite-based fertilizer.

Fig 1: **The Ostara Pearl® Process**

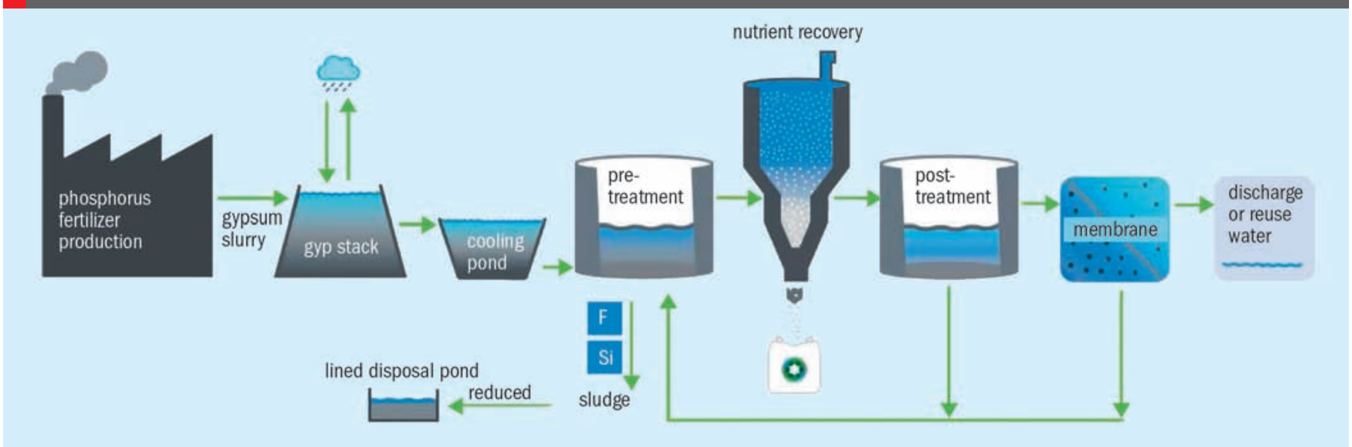


Ostara undertook initial laboratory testing on a variety of potential reagent combinations to selectively remove fluoride, silica and calcium from the pond water while minimising P losses with the associated precipitates. The company ultimately came up with a 3-stage precipitation process, which is capable of removing sufficient amounts of the target components while maintaining about 70% of the P in solution. This pre-treated solution was then available for struvite precipitation.

Ostara liaised with Jacobs Engineering to undertake an 18-month pilot study. Initial experiments yielded very high fractions of fine powdered struvite but with little crystal growth. Further testing showed that there was a relatively narrow set of conditions under which crystal growth would occur with minimal fines formation. This required more accurate control of the pre-treatment conditions in order to reduce the formation of amorphous co-precipitates and to minimise the effects of silica gels.

The process is an adaptation of Ostara's *Pearl*® process, which has been used in municipal wastewater treatment plants since 2007. This comprises a fluidised bed reactor designed for controlled crystallisation and crystal growth of struvite, producing struvite granules in the 100-350 SGN size ranges for targeted markets. Figs. 1 and 2 show a schematic representation of the *Pearl* reactor and process. The blend of fresh wastewater and reagents passes through the fluidised bed of crystals, allowing them to grow slowly over a number of days until they reach the required size. Ostara markets the produced fertilizer

Fig 2: **Ostara pondwater management system**



under the *Crystal Green*® brand on a cost/revenue basis with the client sites.

At the Jacobs pilot facility, once the appropriate pre-treatment conditions were developed and the *Pearl* reactor was optimised for crystal growth, the *Crystal Green* produced was very white, granular and uniform. Chemical analysis showed that it was nearly pure struvite and would meet North American and international fertilizer standards for metals.

The final phase of the process development was to demonstrate that the *Pearl* effluent could be polished to meet a range of environmental discharge and reuse criteria, and to demonstrate that none of the product, by-product or effluent streams showed any hazardous characteristics. The product and by-product solids were tested for total composition analysis (metals and organics), TCLP (Toxicity Characteristic Leaching Procedure) analysis (metals and organics) and other parameters, and none were found to be hazardous or exceed any land ban standards. None of the organic contaminants were detected in any of the analysis performed. Table 2 shows the results for total metals and TCLP metals.

Table 3 shows the water qualities that were achieved using various membrane treatments of the *Pearl* effluent over a two-month operating period.

The success of the pilot scheme to produce both a recovered granular product that meets fertilizer standards, and a treated water quality that could meet any expected environmental discharge and reuse standards in an economically attractive way, led Ostara to secure a contract with The Mosaic Company to develop a demonstration plant of the technology.

On 28 February 2012, Ostara broke ground on this demonstration plant, which is located at Mosaic's Riverview facility in Central Florida. The plant is designed to recover 10 s.tons/day of *Crystal Green* fertilizer from a treated flow of 30-50 GPM of pond water, depending on recovery efficiency and pond water concentrations. The plant is a complete treatment system and fertilizer packaging plant, with on-site storage for up to 160 s.tons of product. The demonstration plant is testing and working to optimise the design and develop the capital costs of a commercial system capable of treating up to 500 GPM of pond water.

Steve Wirtel, Senior Vice President Technology Solution Sales, told *FI* that the Riverview plant has been achieving its water quality targets. The by-product *Crystal Green* fertilizer is being targeted for sale in Florida, where growers have appreciated its slow-release qualities.

Ostara continues to fine-tune the process at the Riverview site, with the aim of achieving competitive operating and capital costs. Ostara president and CEO Philip Abary says that the process will produce dischargeable water for significantly less than the costs of the double-liming alternative, with costs in the low-$20s per 1,000 gallons of processed water, including both capital and operating costs (roughly 50% each).

Once proven on a commercial scale, the Ostara process promises the opportunity to treat and discharge or reuse excess

Table 2: **Ostara *Crystal Green*® product analysis from pilot plant**

Parameter	Total analysis	AAPFCO standards (for 28% P_2O_5)	TCLP result (mg/l)	TCLP (mg/l) standard
Total N	5.3%			
Total P_2O_5	30%			
Total K	0.1%			
Mg	10%			
Arsenic (mg/kg)	13	364	0.19	5.0
Barium (mg/kg)	1.19	n/a	0.02	100
Cadmium (mg/kg)	0.17	280	0.02	1.0
Chromium (mg/kg)	0.31	n/a	0.02	5.0
Cobalt (mg/kg)	0.18	86,800	n/a	n/a
Molybdenum (mg/kg)	0.21	1,176	n/a	n/a
Nickel (mg/kg)	9.2	700	n/a	n/a
Lead (mg/kg)	0.16	1,708	0.03	5.0
Selenium (mg/kg)	0.8	728	0.08	1.0
Silver (mg/kg)	0.06	n/a	0.03	5.0
Zinc (mg/kg)	3.5	11,760	n/a	n/a
Mercury (mg/kg)	-	28	0.00053	0.2

Table 3: ***Pearl*® pilot plant water quality performance**

Parameter	Typical pond water	Pearl effluent	NF effluent	RO effluent
pH	2.1	7.1	6.9	6.3
Conductivity (uS/cm)	22,100	23,600	270	5.8
TSS (mg/l)	22	n/a	0	0
Ammonia (mg/l as N)	1,240	330	3.1	0.29
Fluoride (mg/l)	4,120	41	2.6	0.14
Phosphorus (mg/l)	6,600	390	3.0	0.52

Mosaic's Central Florida phosphate operations fall within an environmentally-sensitive area.

Table 4: **Piney Point Phosphates: pond water performance data**

Constituent	Inlet pond water	ACTIFLO clarifier effluent	Multimedia filter effluent	Double-pass RO permeate	Mixed bed ion exchange polisher effluent
pH	2.8	2.8	2.8	6.3	7.0
Calcium (mg/l)	551	551	551	0.1	ND
Sulphates (mg/l)	5,200	5,200	5,200	0.20	ND
Iron (mg/l)	5.6	5.6	5.6	0.02	ND
Phosphates (mg/l)	1,600	1,600	1,600	0.004	ND
Fluorides (mg/l)	150	150	150	0.54	ND
Ammonia (mg/l)	600	600	600	<1.0	ND
TDS (mg/l)	11,500	11,500	11,500	<15.0	ND
TSS (mg/l)	200	<5.0	<5.0	-	ND

Source: Veolia Water *(ND = Non-detectable)*

pond water volumes on a continuous basis. This will allow phosphate producers to work towards operating with minimum water volumes required for heat balance, as well as reducing the financial liability associated with water volumes and total dissolved solids (TDS) in the ponds. This could combine to reduce fresh water intake significantly in an active plant, reduce final closure liabilities, and generate a source of revenue to fund leacheate treatment at closure, while recovering about two-thirds of the phosphate in the pond water and reducing residual sludge volumes.

Making safe for the future

Veolia Water was commissioned to address the challenging environmental problem that arose at the Piney Point Phosphates site, close to the population centre of Palmetto, Central Florida. Piney Point Phosphates was formerly operated by Mulberry Corporation. Following shutdown in 1999 and the declaration of bankruptcy in 2001, the State of Florida assumed responsibility for the closure of the site.

Part of the reclamation activities involved the removal of 1.2 billion gallons of acidic wastewater containing high levels of P, sulphate, fluoride and ammonia. Activities also included the treatment of the raw pond water to maximise the recovery of high water-quality effluent for discharge to a coastal estuary that flows into Tampa Bay.

N.A. Water Systems, a division of Veolia Water, the *AMDRO*™ technology to treat the complex Piney Point pond water. *AMDRO* is an RO technology operated in double-pass mode. By combining Veolia's proprietary *ACTIFLO*® clarification process with filtration, RO and ion exchange, this unique technology generates high-quality effluent with minimum pre-treatment requirements. The *AMDRO*™ process comprises multiple treatment processes, involving clarification, media filtration, reverse osmosis and ion exchange for polishing.

In the treatment process, the acidified water passed through a solids/liquid separation step, using *ACTIFLO* clarification technology. This process uses microsand as a seed for floc formation. A unique coagulation process designed for acidic conditions was used in the *ACTIFLO* system to enhance the solids/liquid separation efficiency, including removal of algae from the gypsum stack pond water.

The water from the *ACTIFLO* process was then further treated with media filtration to reduce the particulates in the feed water to lower concentrations without pH correction. The pre-treated water was then pressurised through a double-pass RO system to reduce the total dissolved solids and ammonia present in the feed water. The permeate from the double-pass RO system was further polished with mixed bed ion exchange demineralisation to generate high-quality water suitable for discharge and reuse. Table 4 shows the results before and after treatment. ■

Making optimum use of water – the Mosaic story

Table 1: **Mosaic Co. global water withdrawals by source** (2009-11) '000m³

	2009	2010	2011
Groundwater	64,600	57,298	54,374
Surface water	213,258	224,097	207,916
Municipal, industrial and wastewater	1,254	1,737	1,864
Global total water withdrawals	**279,112**	**283,132**	**264,154**

In its 2012 Sustainability Report, Mosaic Co. shows how it is addressing issues of water use in its operations in Central Florida and Louisiana. The primary sources for Mosaic's operations are surface water, groundwater and rainwater. Secondary sources of water include water supplied by local authorities and partially-treated industrial and domestic wastewater, also supplied by local authorities. Surface water withdrawals include once-through cooling water utilised by Mosaic's Louisiana facilities. Table 1 shows Mosaic's water withdrawals by source.

Mosaic operations capture rainfall, a portion of which is impounded and utilised by the various production processes, with some discharged through permitted outfalls at its phosphate facilities. Traditionally, Mosaic has considered captured rainfall use as an alternative water supply, and it is used in part to estimate recycle/reuse water usage rates at Florida concentrate and minerals operations.

Mosaic's Florida operations depend on low total dissolved solids (TDS) groundwater for operational needs. Mosaic's withdrawal and use of surface and groundwater for mining and fertilizer manufacturing is highly regulated, with stringent compliance requirements. The permitting, monitoring and reporting standards are mandated by regulatory authorities, which seek to protect water bodies and associated habitats from degradation and adverse environmental impacts.

Mosaic's Central Florida phosphates operations fall within a district that has been identified as a groundwater resource area of concern. As a result, the standards for use and permitting of groundwater resources are very stringent, and the local regulatory authorities have implemented a recovery strategy, which has included phasing out some historical groundwater pumpage quantities with the district and the development of alternative water supplies.

Mosaic continues to reduce its groundwater use: over the past two decades, the company's Central Florida operations have cut groundwater use by over 50%. Mosaic is liaising with the district authorities to develop other viable, long-term alternative water supplies. In addition, the efficiency with which Mosaic reuses related water streams has increased.

Mosaic has voluntarily and significantly reduced its daily permitted groundwater use in Florida. A new proposed 20-year permit will result in a reduction of approximately 30% in permitted groundwater withdrawals. The permit would reduce annual average consumption over is 20-year life to 55 million gallons/day.

Mosaic is currently developing a long-term water strategy for its Florida operations to conserve water resources and reduce the amount of water impounded for operational use.

Recycling and reuse

Table 2 shows Mosaic's water recycle and reuse percentage rates for its phosphate and potash operations. The recycle rates are based on water utilised in operations from groundwater, surface water, municipal and wastewater withdrawals.

Mosaic captures rainfall, a portion of which is impounded and utilised in various production processes. Some is discharged through permitted outfalls at the phosphate facilities. Captured rainfall is not a regulated permitted freshwater use.

Table 2: **Mosaic water recycle and reuse rates** (%, 2009-11)

Location/division	2009	2010	2011
Mosaic Potash (Canada/USA)			
Belle Plaine	86.0	89.0	89.8
Colonsay	n/a	94.0	93.8
Esterhazy K-1	72.7	83.0	82.8
Esterhazy K-2	67.6	82.0	81.9
Hersey	n/a	n/a	91.0
Carlsbad	n/a	n/a	n/a
Mosaic Concentrates (Florida/Louisiana)			
Uncle Sam	-	n/a	n/a
Faustina	-	n/a	n/a
New Wales	-	93.6	93.3
Riverview	-	93.6	96.2
Bartow	-	95.1	95.7
South Pierce	-	95.1	n/a
Mosaic Minerals (Florida)			
Four Corners	-	96.7	95.7
Wingate	-	93.9	93.9
Hookers Prairie	-	97.1	97.3
South Fort Meade	-	99.7	99.8
Hopewell	-	99.1	n/a

Mosaic's discharges from its phosphate facilities are carefully monitored to ensure compliance with permits and local and state regulations. The phosphate operations in Florida discharge treated surface water and water after processing by advanced water treatment techniques, in compliance with permit criteria. A significant percentage of the total outfall from these operations is from rain water, and discharge rates can vary year-to-year, according to levels of precipitation. Table 3 summarises the total water surface discharge from the phosphate operations in Florida and Louisiana. Mosaic's phosphate facilities in Louisiana have permitted outfalls that discharge water to the Mississippi River. Mosaic's potash operations in Canada do not discharge into off-site water bodies. ■

Table 3: **Mosaic phosphates business unit water discharges** (2010/11)

	Units	2010	2011
Annual outfall discharges	Billion gallons	106.8	47.2
Outfall discharge – annual phosphorus loadings	Tonnes	2,216	1,785
Outfall discharge – annual nitrogen loadings	Tonnes	228	123
Outfall discharge – TSS loadings	Tonnes	9,129	6,388
Outfall discharge – sulphates loadings	Tonnes	27,119	20,872