

# Maintaining Bitterns Infiltration at Solar Salt Operation

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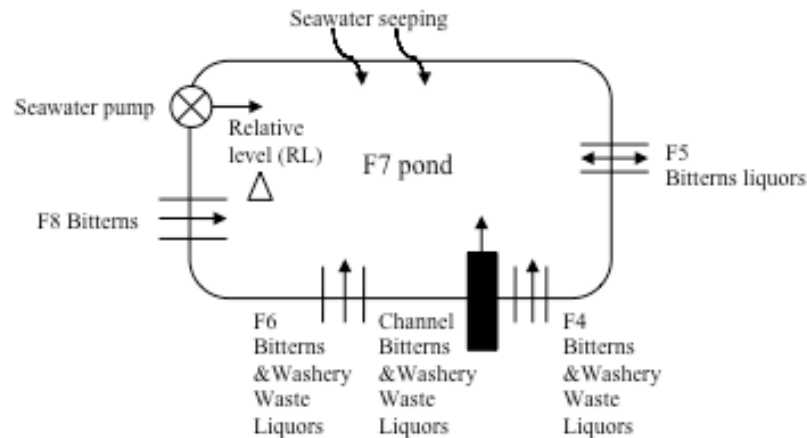
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CEED Client: Shark Bay Resources

## Abstract

*Shark Bay Resources (SBR) operates a solar salt field at Useless Loop in Shark Bay, Western Australia. The current practice for bitterns and washery waste liquors disposal uses a seepage (infiltration) pond system, moving bitterns liquors through disposal ponds, F7 and F5. Crystallisation of sodium chloride, gypsum and an unknown salt structure that has occurred on and below the floor of F7 has caused a decline in seepage rate and infiltration for the past two years. The project seeks to investigate the chemistry of the pond system and the physical conditions at which the crystallisation occurs. One of the objectives of the project is also to find out the depth of the crystal structure and characterize the crystallisation occurring in the underlying strata beneath the base of the pond. X-ray diffraction (XRD) is being used for sample analysis with access from Centre for Microscopy, Characterisation and Analysis (CMCA). The results obtained from XRD will provide a quantitative analysis of the amount and type of crystals present. These results will serve as a guideline for future approaches to determine the porosity and permeability mechanisms in the pond system and possible practical solutions to maintain the current infiltration practice.*

## 1. Introduction

The solar salt operation at Useless Loop consists of a series of primary and secondary concentrator ponds, flume, crystallisers, bitterns liquor disposal ponds, washing plant and ship loading facility. Seawater is fed through an intake gate into the first primary concentrator pond and transferred inland through successive primary ponds. The pump stations regulates the flow of concentrated seawater from the last primary pond into the flume. Concentrated seawater flows through the flume by gravity into the secondary concentrator ponds where it further concentrates as feed brine. Feed brine flow into the crystallisers for initial salt precipitation. The remaining liquid is known as bitterns. Bitterns are periodically replenished with fresh feed brine to off-set evaporative losses. After salt layers are crystallised across the surface of a crystalliser, the bitterns are drained from the crystalliser into the bitterns liquor disposal ponds. Salt is then ripped, harvested and transported to the washplant for washing with seawater to meet its specification limits. Washed salt is then transferred to the stockpile for ship loading and final analysing. Washery waste liquors from the wash plant flow through a series of channels before entering the bitterns liquors disposal ponds for infiltration.



**Figure 1 A Description of the Physical External Structures of F7 Pond with Flow Directions from Several Inputs**

Three major inputs flow into bitterns liquor disposal ponds, F7 are summarised below and as shown in Figure 1:

- the fresh seawater pumped during peak season;
- the inflow of washery waste liquors (high in Calcium) from the washing plant throughout the year;
- the inflow of bitterns (high in Magnesium) from the crystallisers, F8, F4 and F6 during peak season.

The resultant mixtures of all three inputs, known as bitterns liquor, have high levels of calcium and magnesium ions, which may create ideal conditions for rapid crystallisation of salt, gypsum and possibly other unknown compounds.

Bitterns liquor infiltration is vital in enabling SBR to dispose of bitterns liquor sustainably via ground seepage, complementing the overall solar salt operation management procedures. However, F7 has suffered a rapid decline in the seepage rate since 2010. A layer of crystallised gypsum and salt has been found forming across (and possibly below) the entire floor of F7, which is most likely to be the cause of the problem.

The aim of the project is to identify the type of crystallisation occurring and the physical properties under which it occurs (e.g., conditions and depth) above and below the pond floor. The current practice provides a huge cost saving to the whole operation and also minimises the environmental impact to the marine environment of the United Nation (UN) World Heritage Area of Shark Bay. This is especially beneficial in comparison to the use of a direct ocean discharge method. The project will provide an insight into design ideas for practical solutions to maintain infiltration sustainability.

## 1.1 Literature Review

Solar salt evaporation utilises the natural mechanical and thermal energy sources (wind and sun) to produce near to pure salt crystals which can be recovered from seawater. It is favoured in regions with relatively low humidity, high evaporation rates and low precipitation. Concentration and evaporation (crystalliser) ponds are constructed to collect and evaporate seawater from the ocean. They initiate the precipitation of calcium compounds from solution by increasing the salinity of the brine. Excess sulphate crystallises from the brine as gypsum, which is then pumped into crystalliser ponds for salt crystallisation. Bitterns is the remaining

liquid with high magnesium-content and a specific gravity in excess of about 1.25 after around 77% of the salt has crystallised in the crystalliser (Kogel et al.).

The principal ions in seawater brines are  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  (Holser, 1979). Concentrated brine from seawater contains ions in the following weight ratio (Sonnenfeld et al., 1989):  $\frac{\text{Na}_2}{\text{Ca}}=13.2$   $\frac{\text{K}_2}{\text{Ca}}=0.475$   $\frac{\text{Mg}}{\text{Ca}}=3.18$ . Concentration of brines can be measured using the empirical Baume ( $^{\circ}\text{Be}$ ) scale or specific gravity with a reference fluid, where water is commonly used. Method for calculating evaporation rates of brine for solar salt production is provided by Akridge (2007) using a modification to the standard Penman (1948) equation to determine evaporation from open water sources.

Seawater dissolved solids consists of  $\sim 3.6\%$  of calcium sulphate and  $\sim 78\%$  of sodium chloride. The precipitation of gypsum occurs when the volume of a seawater basin is reduced by 66% via evaporation. The order of precipitation of minerals (Kogel et al n.d.) is such that calcium carbonate is the first to precipitate, followed by gypsum and anhydrite, halite, magnesium sulphate and potassium salts.

Modern solar salt production is designed to enhance conservation of the environment, ideally becoming part of an integrated natural ecosystem. Biological processes in natural hyper saline ecosystems are driven by microorganisms which cause a chain of reactions oxidising and reducing key elements, especially in sediments where reactions can proceed fully to an end point. In comparison to many environmentally engineered systems (e.g., natural wetlands used for waste water management), modern saltworks have no chemical contaminants or fertilisers from agricultural usage (Korovessis and Lekkas, 2009) and are thus considered to be a very sustainable practice.

## 2. Methodology

### 2.1 Sample Collections and XRD Calibration

The first sampling was carried out in April 2013 where samples were taken of crystallised gypsum, sand mixtures and bitterns liquors near the shallow part of the edge of F7 and its surrounding ponds for a preliminary test run using XRD. The sampling sites are indicated in Figure 2 (Google Earth, 2012). The result from XRD is tabulated in Figure 4.

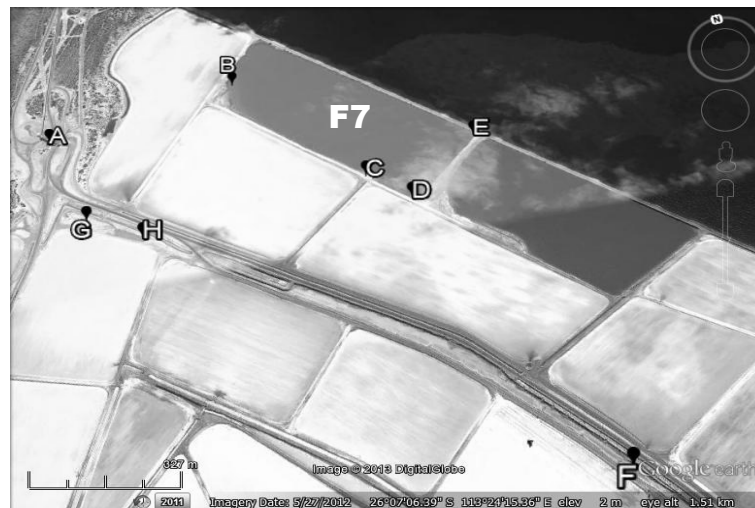


Figure 2 Sampling Site around Useless Loop in April

We also prepared a standard reference batch of samples made from quartz (sand) with known concentrations of gypsum to test for the calibration of XRD. 10 reference samples were prepared with decreasing order of weight fraction of gypsum concentration from 10 wt% to 0.1 wt%. Another 3 reference samples were also prepared which consisted of pure quartz, pure gypsum and pure calcium carbonate respectively. Each sample weighed 30g in total and was further sub-sampled into smaller size after grinding in a ring mill mechanical grinder. In general, quartz acts as an internal standard to differentiate between crystalline and amorphous materials present within the sample. XRD was then run on all standard samples to ensure its accuracy and precision in identifying the peak patterns as diffracted by the crystalline phases in each sample.

Core sampling was executed in September 2013 by a team led by Professor Paul Lavery and Dr. Oscar Serrano Gras from Edith Cowan University (ECU). 12 sediment samples from 12 sites in F7 were collected using percussion-hypodermic coring (1.5 m-long liners made of high-pressure PVC). The length of the sediment samples recovered range from 72cm to 110cm. Each core was divided into 2 hemi-cores with a total of 24 hemi-cores. The hemi-cores will be subsampled after visual inspection and determination of the different coloration and gypsum variation layers present. The subsamples will be evaluated by XRD for quantitative analysis.

## 2.2 X-ray Diffraction

To evaluate the phases present in the crystallised layers of gypsum and salt, XRD is used with access from CMCA. Powder XRD is a method used to investigate and quantify the crystalline nature of materials by measuring the diffraction of x-rays from the planes of atoms within the material. A beam of X-rays strikes a crystal and diffracts into many beams in specific directions. The angles and intensities of these diffracted beams give the lattice spacing which will identify the crystal structure. The equipments and resources available in CMCA include the PANalytical Empyrean multi-purpose research diffractometer and a powerful software package, HighScore Plus for peak search and phase identification.

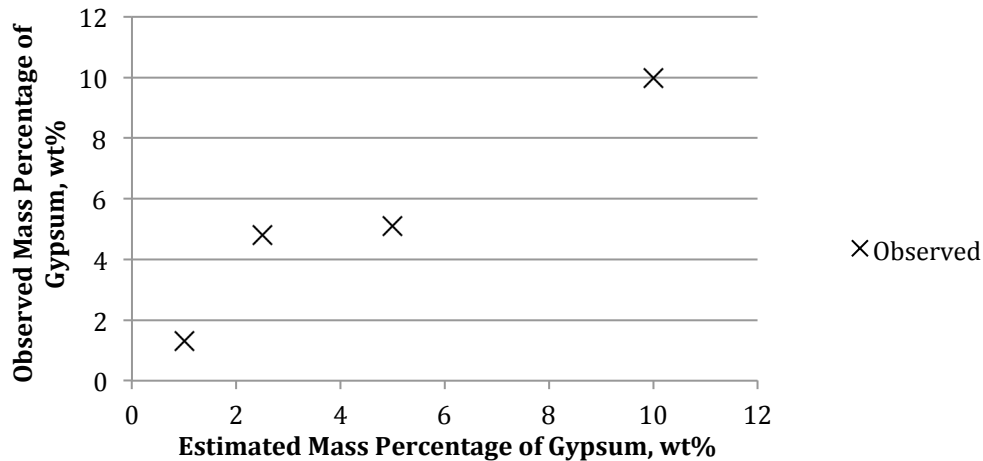
Powder XRD samples for quantitative analysis have four preparation stages, which are drying, grinding, addition of internal standard and micromilling. The samples need to be fine grained to achieve good signal-to-noise ratio, avoid fluctuation in intensity and avoid spottiness and minimize preferred orientation. The samples are prepared in recommended size range around 1-5 $\mu$ m (Rudman, 1999). Samples are ground into fine powder using a ring mill in the crushing workshop provided by UWA Geotechnical facility.

Random mounts are preferred for identification of phases in the samples. Particles ground to 1-5 $\mu$ m are packed to a flat surface onto a sample holder to assume preferred orientations and ensure reflections. The sample holder is rotated throughout the process to improve the measurement statistics.

Evaluation of data analysis from XRD is done by peak identification and phase identification (Klug and Alexander, 1974) using HighScore Plus which supports Rietveld's refinement. The first part involves background subtraction, smoothing, peak search and profile fit. Random noise contributions from air scattering and the presence of amorphous phases to the peak patterns can be reduced using these refinements. The second part involves application of a reference database of characteristics of known powder pattern as a fingerprint to identify the phases present. Experimental XRD data are compared to reference patterns to determine what phases are present in the samples. Specimen displacement error will cause a shift in peak

position. XRD data is a good match if a major reference peak is observed. Often minor reference peaks could be lost in the background noise.

### 3. Results and Discussion



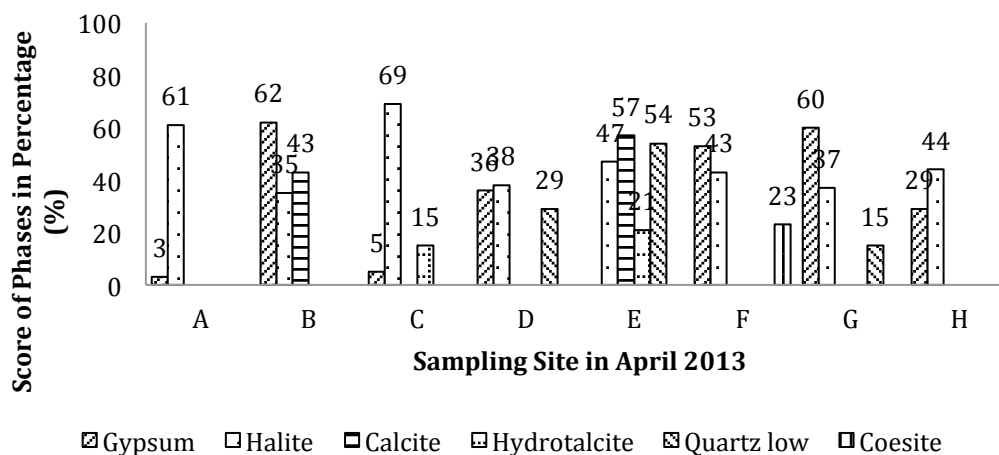
**Figure 3** Calibration Graph of Estimated and Observed Mass Percentage of Gypsum from the Analysis of Standard Reference Samples

The result from the analysis of standard reference samples is shown in Figure 3. The x-axis represents the mass percentage calculated from standard sample preparation, while the y-axis represents the mass percentage determined using XRD. From the figure above, the outlier in the observed pattern is most likely due to human error during sample preparation. The possible contributions to the outlier may be incorrect position of the powder sample in the sample holder, tightness of the packing of sample into the holder and insufficient Rietveld refinement process.

The data analysis from the standard reference batch of samples showed that the limit of detection of XRD is around 1% mass percentage of the phase present. Phases with concentration lower than 1% are less likely to be detected and quantified by XRD.

In some of the samples, the peak pattern of gypsum was not detected in the major reference peak, which indicated that the random orientation and structure of gypsum in its natural form may have been destroyed due to excessive grinding of samples in the preparation stage. We have therefore decided to limit the period of time used for grinding of each sample, to less than 1 minute to prevent disruption and phase change in the sample. A recalibration of standard reference will be repeated by preparing triplets of samples for each concentration of gypsum at 1 wt%, 2.5 wt%, and 5 wt%. Grinding time will be reduced to 45 seconds. This will help to identify the possible cause of the outlier from the first calibration experiment.

Peak patterns from the analysis of pure gypsum, pure quartz and pure calcium carbonate samples achieved satisfactory results where the theoretical model matched most of the pattern list of the observed model. This indicates that the phases are mostly crystalline and can be detected by XRD.



**Figure 4 Comparison of Score of Phases in Percentage using XRD for All Samples from the Sampling Site.**

## 4. Conclusions and Future Work

XRD data analysis has identified the presence of gypsum, halite and calcite as the major phases present in the samples from F7. The quantitative analysis of the phases present in the core subsamples will enable us to consider further investigations which could include physical modelling on the pond system to test for porosity and permeability. The outcomes from the project will provide a better understanding of the crystallisation beneath the pond system and introduce guidelines for possible future investigation into the practical solution in maintaining the infiltration of bitterns.

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