Successful Passive Treatment of Sulfate Rich Water

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Abstract

A passive sulfate reduction system with iron scrubbers was identified as the most viable option for treatment of elevated sulfate within leachate from an old landfill and bench scale trials were established in 2019 at the site to test the theory. This included the use of Biochemical Reactor (BCR) with different proportions of wood chips, straw, manure, limestone, and biochar to culture sulfate reducing bacteria. In addition the concept of 'bugs on booze' was trialled, using Fix Bed Anaerobic Bioreactor (FBAR), where alcohol added to enhance the sulfate reducer activity. In total three BCRs and two FBARs were set up for this stage of the assessment. The resulting treated leachate was then passed through different iron media types (haematite, magnetite and iron filings) to remove sulfide generated by the bacteria, with an aerobic wetland used to polish the effluent. The success of the bench scale project led to a pilot scale system being constructed and monitored in Spring 2020, the results of which confirm the success of the bench scale testing and provides useful insights into management of the system particular in winter months. The COVID crises has had its impact but the system has operated continuously and will run through 2021.

Keywords: Passive Treatment, Sulfate Reduction, Biochemical Reactor, Wetland, Pilot Plant

Introduction

SLR Consulting (SLR) was appointed by British Gypsum (Saint-Gobain Construction Products UK Ltd trading as British Gypsum) to investigate options for the treatment of leachate emanating from an old landfill disposal site at their property in East Sussex. The options analysis undertaken by SLR highlighted a passive treatment option for the removal of the sulfate, to below discharge standards, was a potential option but that it required treatability/feasibility testing. The concept involved the use of naturally occurring material containing sulfate reducing bacteria to remove the sulfate with the resulting dissolved sulfide in the water being 'scrubbed' by an iron oxide filter. An aerobic wetland would then be used to polish any final effluent before it is discharged. The design of the system was undertaken with Linkan Engineering who also supervised the construction and commissioning of the system with support from SLR.

The Treatment Process

When the design of a treatment system is necessary, its design would be based on the results of a "staged process" of bench and pilot-scale testing. Typically flow rates of c.5 to 10 mL/min or less are termed "bench-scale" with "pilot scale" test as one that would treat about 4 L/min or more.

Bench scale testing is an effective way to advance a project toward to full scale implementation while gaining useful knowledge about appropriate media, reaction rates, and functionality that increase confidence and overall effectiveness. The overall footprint may be reduced from outline design stage, which leads to lower capital costs and maintenance. The typical passive biological treatment process for sulfate reduction utilizes an anaerobic Biochemical Reactor or BCR. While BCRs receiving Mining Impacted Water (MIW) may be configured as "up-flow" or "down-flow", experience has shown that up-flow BCRs are better than down-flow BCR in treating sulfate rich and metal poor leachates. The system is required for such a water which is being generated by a closed landfill.

The organic substrate comprises hard wood chips, limestone, straw and biochar in varying proportions. 0.1% animal manure is added to provide the naturally occurring sulfate reducing bacteria. The sulfate in the influent leachate is then consumed by the bacteria and produces sulfide:

$$SO_4^{2-} + 2\,CH_2O = H_2S + 2\,HCO_3^-$$

Usually when such systems are used the dissolved metal ions in the mine water react with the sulfide to precipitate insoluble metal sulfides in the wetland/BCR substrate. The lack of suitable metals in the British Gypsum discharge requires a metal ion was needed to be added passively to sequester the sulfide generated through the sulfate reduction process. The dissolved sulfide will precipitate as an insoluble metal sulfide or potentially as free sulfur. For example, at the British Gypsum site, iron was added at bench scale via a treatment substrate such that the following reaction (through precipitation of dissolved iron or on metal iron surfaces), in the substrate will occur, shown simplistically below:

$$Fe^{2+} + S^{2-} \rightarrow FeS$$

Sulfur sequestration is the primary problem with a sulfate-only BCR. While minor amounts of native sulfur will accumulate on the surface of an up-flow BCR, experience has shown that the BCR effluent, bearing dissolved sulfide ion (HS-), needs to be scrubbed with an inexpensive sacrificial metal. This metal can be either in the zero-valent state such as scrap iron, or as an oxide. However, care in media selection is warranted. An Aerobic Polishing Wetland (APW) is also a lined shallow pond filled with soil and locally harvested or cultivated

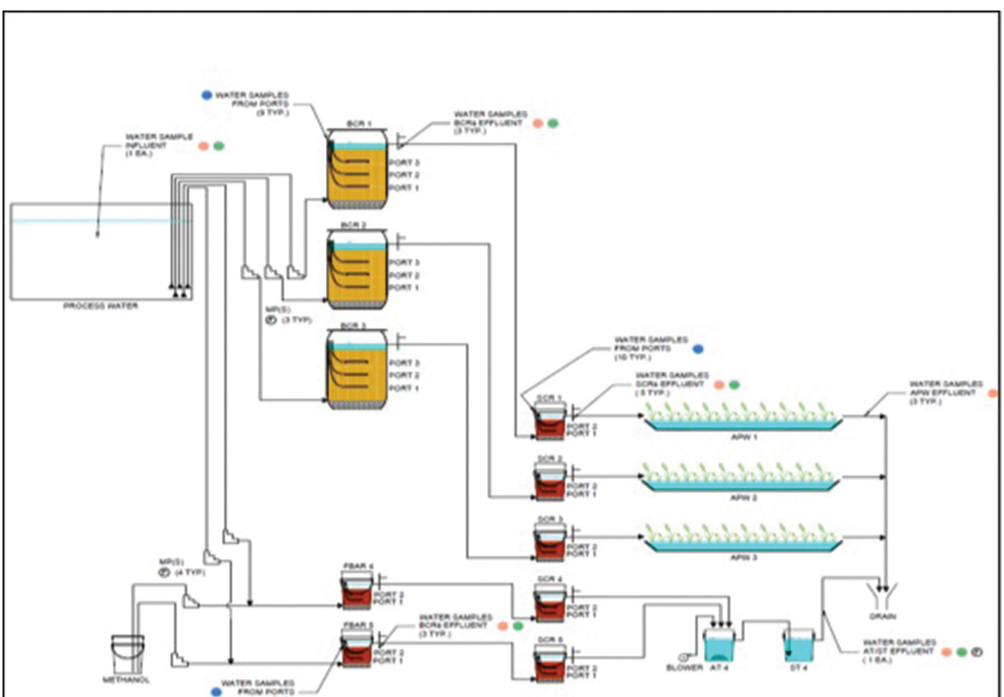

Figure 1 Bench Scale Test Flow Diagram.

vegetation (if available). The purpose of this process feature is to re-aerate the anoxic effluent from the BCR.

Bench Scale Set Up

To test the theory of a passive wetland treatment solution, a bench scale system was set up at the site to run for 20 weeks. The bench scale system comprised:

- 3 No. Biochemical Reactors (BCRs) – pump fed, each filled with a different test mixture comprising different proportions of manure, wood chips, hay, limestone, and biochar.
- 3 No. Sulfide Scrubbers (SCR), each filled with a different test mixture comprising magnetite, hematite, and iron filings.
- 3 No. Aerobic Polishing Wetland (APW) cells planted with wetland plants from the site; and
- 2 No. Fixed Bed Anaerobic Bioreactors (FBAR) with 2 No. Sulfide Scrubbers, Aeration Tub and Settlement Tub.

A conceptual layout of the process units used in the bench scale test layout is provided in Figure 1. As part of the treatability, it was also decided to consider the use of a hybrid-passive approach which involves the additional of a soluble form of hydrocarbon such that the bacteria would react more quickly that the less soluble forms held in natural organic matter such as sawdust/manure. In this Fixed Bed Anaerobic Reactor (FBAR) small quantities of ethanol is added to a small system to provide a food source for the bacteria. The reasoning being that with a more soluble food source the bacteria will consume more of the sulfate and hence less area will be needed for the treatment at pilot and full-scale. This also has an active aeration and settling tank in replacement of the aerobic wetland system to act as a comparison.

Monitoring and Results

The system was monitored for a variety of analytes along with the flows throughout the system, Weekly field-based monitoring of pH, redox and conductivity was undertaken along with sulfate, sulfide, nitrate, calcium and magnesium. At monthly intervals, phosphate, alkalinity, hardness, iron, nickel, zinc and total organic carbon (TOC) was analysed. The flows through the reactor were typically 6 L/d for the BCRs and 25 L/d for the FBARs. The latter was also reduced at the end of the treatment to be closer to the BCR flow rate to act as a comparison. The process flow diagram for the system is shown above in Figure 1 and this shows not only the flow process for each of the treatability tests – but also the location and frequency of the sampling of the various parts of the system to assess the treatment progress over time. The monitoring of the system was undertaken at weekly intervals where the redox and pH of the various components coupled with the flow rates were taken. The sulfate and other components were analysed at an offsite UKAS accredited laboratory. The results of the treatability study are shown in Figures 3– 6.

The bench scale test results indicated that both BCRs and FBAR treatment will produce an effluent that would meet a 250 mg/L sulfate limit. In mine water treatment systems sulfate reduction rates typically range form 0.1 – 0.3 moles/m3 substrate/ day. The rates for this study are shown to be at the upper end of this range. In addition, the FBAR rate of sulfate reduction was c.15 times that of the BCR reduction rate. Consequently, the media volume required to accomplish this with a

BCRs and SCRs 1 - 3 *FBARs, SCRs and Aeration* *Aerobic Polishing Wetland*

Figure 2 *Bench Scale Test Set Up.*

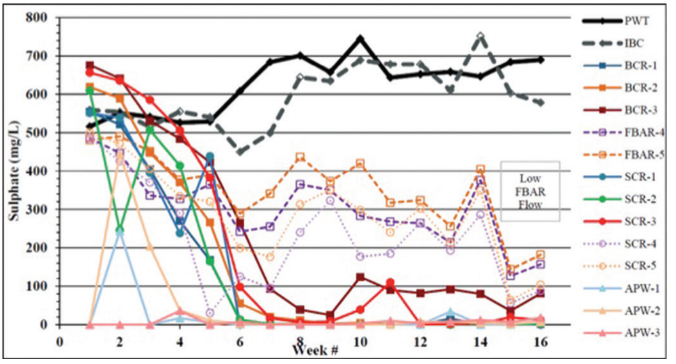

Figure 3 *Sulfate Concentrations.*

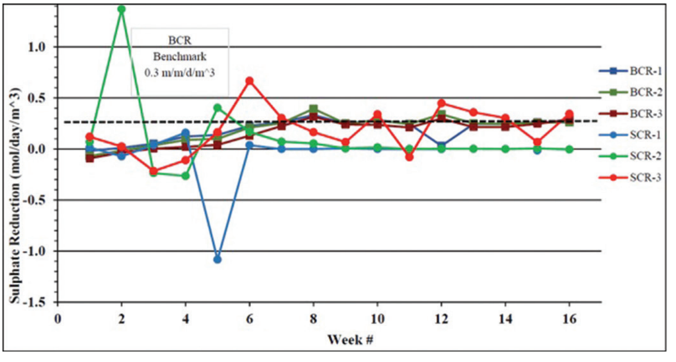

Figure 4 *BCR Sulfate Reduction Rate.*

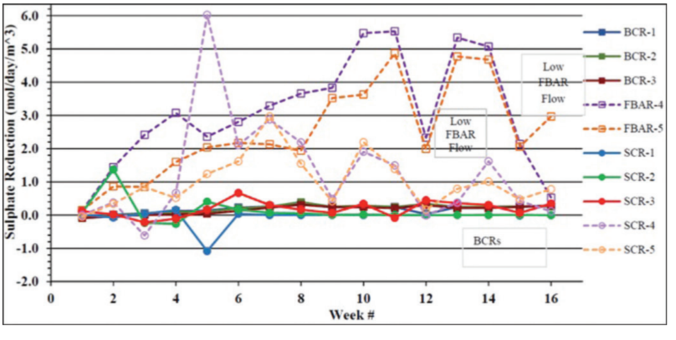

Figure 5 *FBAR and BCR Sulfate Reduction Rate.*

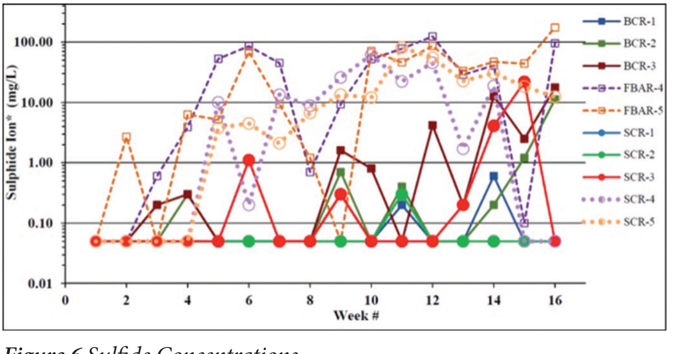

Figure 6 *Sulfide Concentrations.*

BCR will be c.15 times greater than for the media volume for an FBAR with an identical treatment capacity. The land area footprint required for an FBAR treatment unit would therefore also be 15 times smaller than that required for a BCR. However, the FBAR process will require the delivery of a steady and reliable supply of alcohol as a microbial nutrient.

The BCR process does not require addition of nutrient, as alcohol, and therefore is seen as more passive aside from pumps to move the leachate to the treatment system. The scrubbers sequestered sulfide ion present in the BCR and FBAR effluents. However, the bench scrubbers that received the FBAR effluents, proved to be undersized. The aerobic wetland system was effective in removing the iron leached from the scrubbers and did have a positive impact on the organic carbon which came through the system. The results of the bench scale testing were very encouraging. This has led to the design and development of a pilot scale system at the site.

Pilot Scale Testing

The success of the bench scale trials led to the design and installation of a pilot scale system in Spring 2020 on the site. The purpose of the system was to confirm the success of the bench scale study by using the sulfate removal coefficients and preferred media option. The latter comprised mixing of wood chips, biochar, limestone, wheat straw, bench scale organic material and goat manure inoculum. The desired flow being introduced into the system was 0.5 L/min and above and there was no additional of alcohol as nutrient. The bench scale testing showed that free sulfur was generated in the BCRs and FBRs and hence the scrubbers were not required. However, the pilot scale system allowed addition if the system required additional sulfide removal. Conceptually the pilot scale system had the original orientation of sequential treatment, although three biochemical reactors were established such that variety in flow rate and other parameters can be used to test the system. To construct the pilot plant, available

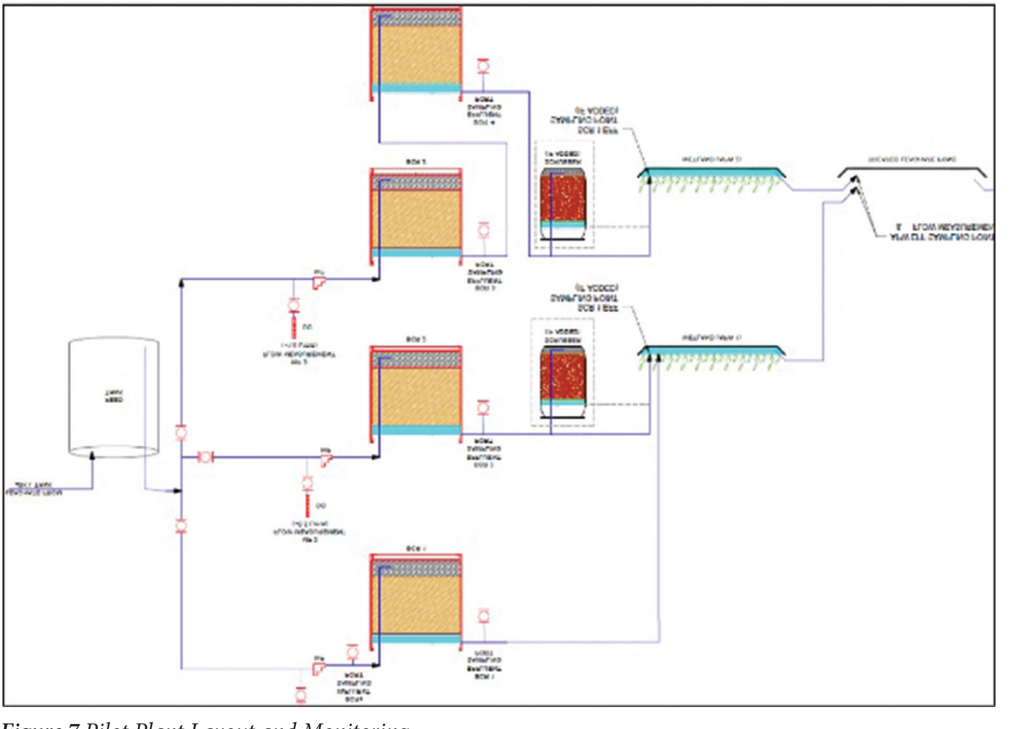

Figure 7 *Pilot Plant Layout and Monitoring.*

Figure 8 Passive Treatment Pilot Plant from right to left (Feed Tank; BCR1, 2, 3, 4; Reed bed (APW) 1, 2, discharge holding pond showing purple/white bacteria).

infrastructure was used. Cargo containers were used for the three BCRs. These were waterproofed and lined with insulation on the base and sides and reinforced such that they could hold the substrate and the water. Sampling ports were established such that different horizons in the units could be analyzed if required. The aerobic polishing reed beds was designed with baffles to lengthen the flow length in the wetland and was designed for the removal of BOD/TOC. Facility was also made to add on the iron-based sulfide sequestering unit should monitoring indicate that sulfide is leaving the system at concentrations which were unsustainable from an environmental perspective.

The pilot system became live through a commissioning phase in Spring 2020 before the COVID emergency, and monitoring was undertaken by a skeleton staff on site since. A number of sampling points were included in the system including redox zone depth measurement in the anaerobic material, along with the treatment zones at various locations along the system.

The results of the ongoing monitoring have indicated good sulfate removal with no sulfide detectable in the effluent. Free sulfur has been identified in the system which has the potential to oxidise and release stored sulfur as sulfate, although during the summer/spring there was no evidence this has occurred. Elemental sulfur may be the primary product of sulfate reduction in the BCRs. Evidence includes the white cloudiness in the BCR effluents, white deposits in the wetland influent zones, and the purple tinge (likely the bacteria Chromatium sp. and Chlorobium sp.) in the final pond influent zone (Figure 8). Purple sulfur bacteria produce elemental sulfur as part of their life cycle. Thus far the pilot cell is confirming the results of the bench scale testing with latest influent sulfate of c.800 mg/L being reduced to c.100 mg/L in the effluent, thus providing robust design data for the full-scale system. The first seven months of sulfate removal are shown in figure 10. In the winter months the treatment efficiency decreased believed to be temperature reduction and potential free sulfur oxidation. This temperature dependency is a relatively well-known phenomenon with passive systems, with sulfate reduction rates improving in spring and some months. This aspect of the pilot scheme has been very useful in guiding potential management changes which may need to be included in winter months to maintain the same reduction in sulfate. The sulfide remained non detected in the discharge and the BOD/TOC, after an initial stabilisation period, was recorded as c.10 mg/L. A full scale aerobic wetland will remove the BOD/TOC with greater efficiency. Notwithstanding the performance of the BCRs was reduced over winter months and this was investigated. The monitoring showed some interesting changes in redox and TOC in the leachate entering the treatment system.

Landfills are large anaerobic digesters, and this can result in inconsistent performance (effluent) from the treatment system. Influent TOC 'food' (that is' digestible' for the pilot BCR organisms - like a 'bugs on booze' system) sustain the BCR well. When this food is reduced quickly in the leachate, the

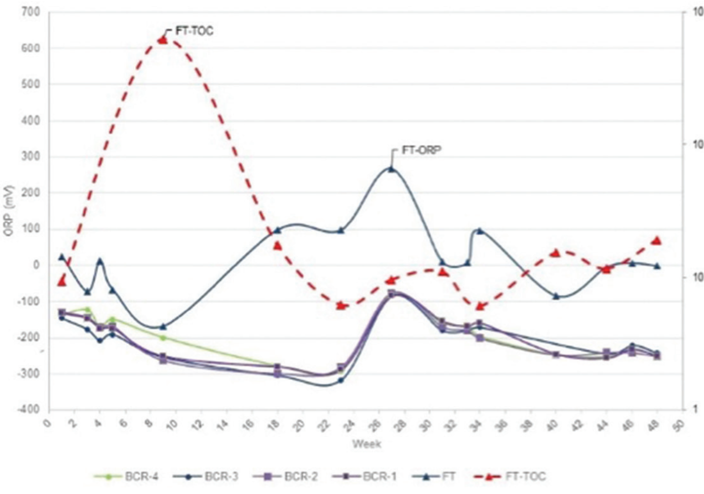

Figure 9 *Results of TOC and ORP.*

whole biosystem in the BCRs is essentially put on starvation mode with knock on lower sulfate reduction rates. The TOC levels are reinforced with the redox reading in the influent water as shown in Figure 9. This is very useful information as it might suggest soluble organic matter amendment (as used in the bench scale testing) may be required during the winter months if the sulfate treatment is shown to fall below established permit conditions.

The pilot system is still in operation (March 2021) and the intention is to operate the system through the summer and winter of 2021 with results reported by the end of 2021. Notwithstanding additional data will be produced as the COVID emergency and lock down is lifted.

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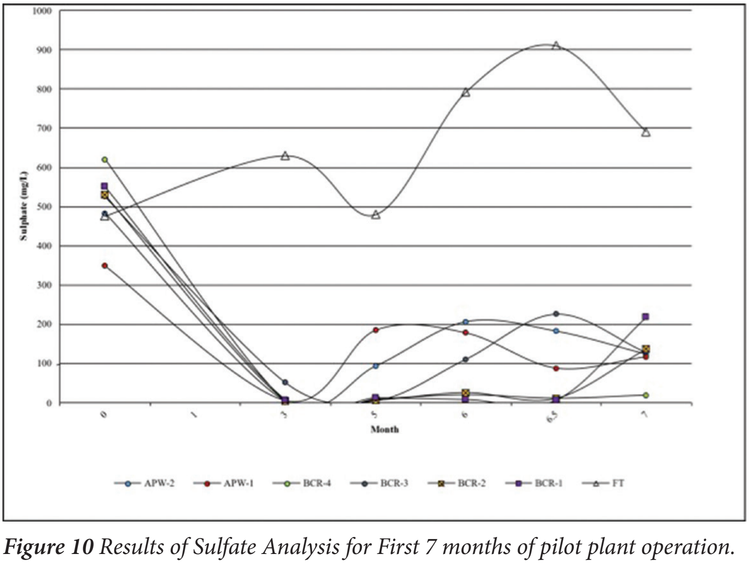

Figure 10 *Results of Sulfate Analysis for First 7 months of pilot plant operation.*

Passive Mine Water Treatment Trials of Dispersed Alkaline Substrate at Two Emblematic Mine Sites in Wales

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Abstract

Mine drainage from abandoned mines is a serious environmental legacy in Wales. Passive treatment is an attractive remediation strategy, but it has often failed due to premature clogging or passivation of the systems.

The Dispersed Alkaline Substrate (DAS) treatment system, based on a fine-grained alkaline reagent mixed with wood chips to enhance the porosity, was developed to overcome these problems and is successfully deployed full-scale at two sites in SW Spain. In Wales, where the climate is more maritime, the system is being tested at two emblematic metal mine sites, Parys Mountain and Cwm Rheidol, which are two of the top five most polluting mines in Wales.

Field and laboratory trials started in late 2020/early 2021. The preliminary results from the trial at Cwm Rheidol and initial results from the column tests completed on Parys Mountain mine water at the University of Huelva are presented here. Calcite-DAS combined with MgO-DAS remove Fe, Al and divalent metals to low levels, while calcite-DAS combined with $BaCO_3$-DAS additionally also decreases sulphate concentrations and calcium (hardness).

Keywords: Passive Treatment, Divalent Metals, Sulphate Removal, Clogging, Passivation

Introduction

Wales has a long history of metal mining, dating back to the Bronze Age. By the 1920s most mining of metals had ceased, however drainage from in excess of 1,300 abandoned metal mines continues to impact over 700 km of river reaches today. Passive treatment systems, which only require naturally available energy sources and infrequent maintenance, can be an economical and sustainable option to decontaminate these mine waters. Nevertheless, they are prone to clogging and passivation (loss of permeability or reactivity) when used to treat mine water with high metal concentrations or high acidity loads.

To overcome these constraints, the Dispersed Alkaline Substrate (DAS) was developed (Roetting *et al.*, 2008a, 2008b, 2008c, Torres *et al.*, 2018), which consists of a fine-grained alkaline reagent (e.g., calcite [$CaCO_3$], caustic