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Chemical process development of Sorel cement from seawater bitterns using TRIZ methodology

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Abstract:

The primary goal of the project was to develop a Portland cement replacement with a lower carbon dioxide footprint for use in building construction in Bangledesh. The MCC process concentrates and purifies the bitterns to produce a magnesium chloride solution that is dehydrochlorinated to produce magnesium oxide. The TRIZ toolbox proved invaluable in accelerating the development of a magnesium oxide process. Analysis of the proven spray reactor technology identified complications. After the initial chemical reactor concept was radically changed, it was demonstrated with pilot plant testing. Analysis shows this process has a significantly smaller carbon dioxide footprint than that of Portland cement. Functional analysis proved to be a critical tool along with others in TRIZ tools.

Introduction

Magnesium oxychloride cement [1] (MOC), Sorel cement, is gaining renewed interest as a means to lower the carbon dioxide footprint relative to Portland cement for building construction in Bangladesh. Sorel cement is the reaction product of magnesium oxide and magnesium chloride. The Mennonite Central Committee of Bangladesh (MCC), a nongovernmental organization (NGO), has been developing a water resistant MOC formulation known as Ricestone®, using rice hull ash as an additive. Several buildings have been constructed of this material using block walls and organic fiber reinforced roof panels have been constructed.

Feasibility Analysis

Salt farming, producing salt from evaporating seawater, results in a concentrated waste brine known as bitterns. This material is rich in magnesium chloride and other salts [2]. Recovery of magnesium from various brines has been practiced for many decades. The starting point in the analysis was the Aman process [3] (described later) developed in the 1940s to recover magnesium hydroxide from Dead Sea brines. Considerable work has been done on recovery of chemicals from the Great Salt Lake (Utah, USA) [4,5].

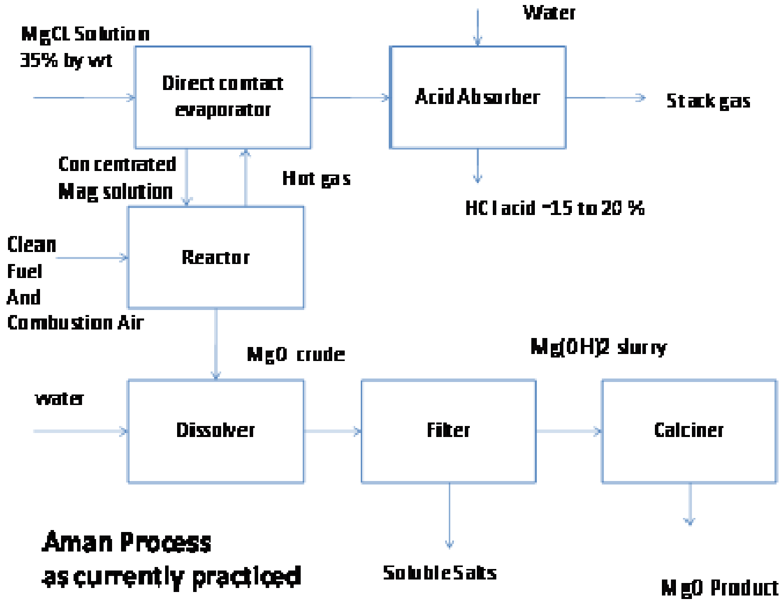

Figure 1. Block Diagram of Aman Process

The Aman process, shown in Figure 1 as a block diagram, starts with the concentrated purified brine. The concentration and purification process removes sodium chloride, potassium chloride, and sulfates in the form of calcium sulfate. The high temperature reactor is the heart of the process, The reactor dehydrochlorinates magnesium chloride to produce magnesium oxide and hydrogen chloride. The hydrogen chloride recovered is an aqueous acid of modest concentration. Purification of the reacted solids removes the last traces of soluble salts to produce a very high purity salt-free magnesium oxide suitable for industrial refractory [6]. Since MOC does not require this purity, Figure 2 shows the block flow diagram of the main steps.

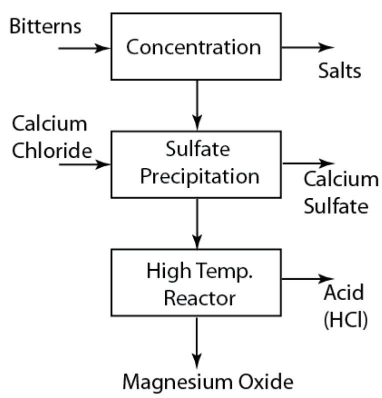

Figure 2. Simplified block flow diagram for magnesium oxide production for MOC

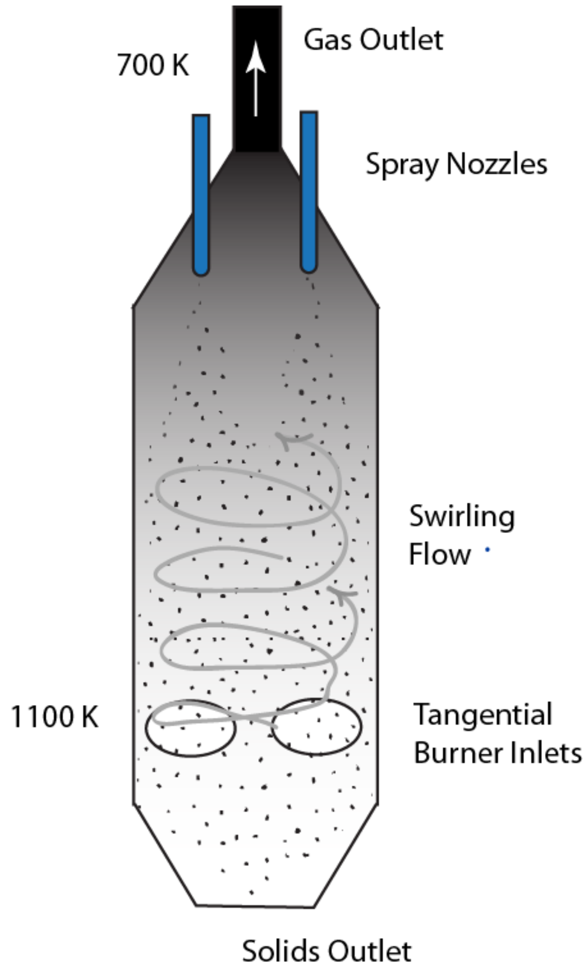

Figure 3. Cross-section schematic of spray pyrolysis reactor

An illustration of the Aman process reactor shown in Figure 3 is based on the patent description and information from the company's web site [5]. Concentrated magnesium chloride solution is sprayed downward into a hot reactor vessel. A counter-flowing hot gas stream evaporates water, heats the downward falling drops, and causes the dehydrochlorination reaction to produce the product. The process challenge with this reactor design is the transfer of the energy necessary for the endothermic reaction. This is accomplished by providing sufficient drop surface area and temperature differential between the gas and spray drops. The design conflict simply stated is: if the drops are too small, they will be entrained; if the drops are too large, they will not react completely. Entrained drops are scrubbed downstream and recycled back to the reactor. This increases the size of the complex costly highly corrosion resistant scrubber equipment. This is a physical contradiction representing one framing of the design issues.

This reactor technology is highly complex, involving three phases, solid, gas, and liquid. The expected operational envelope is narrow and constrained by the up flow gas velocity and the drop size range of the spray. The counter flow of solids and gas shrinks the operating window. Solids build-up on walls is a common problem with 3 phase reactors, such as an entrained-flow slagging coal gasification reactor. The combination of factors indicates a reactor very difficult to operate on a large commercial scale and impossible to scale-down for feasibility tests.

Functional analysis

The reactor technology was challenging because of the complexity of the system, the mechanical design, and operational issues. Highly concentrated salt solutions containing hydrogen chloride in the reactor scrubber system are extremely corrosive to the reactor scrubber system and spray system. High temperatures (150^{o}C), aqueous hydrochloric acid, and high salt concentrations make materials selection difficult, prohibiting all but the most exotic and expensive alloys. The equipment requiring expensive materials of construction include process vessels, pumps, piping, valves, and spray nozzles.

The functional analysis of the Aman reactor system is shown in Figure 4-A. The core design conflict is centered around droplets that result in adverse functions as shown in the diagram. In this functional diagram, the drop object is an auxiliary tool. The primary process innovation was to eliminate this auxiliary tool (drop) which eliminated the need for the spray nozzle.

The remaining resources were reformulated to yield the process shown in Figure 4B in function form and Figure 5 in block diagram form. The proposed process was to blend magnesium chloride solution with a recycle portion of magnesium oxide to form a solid material. This solid material could be processed in a conventional furnace, either continuous or batch, to produce the final product. A patent search identified an expired patent with teachings useful in the process development.

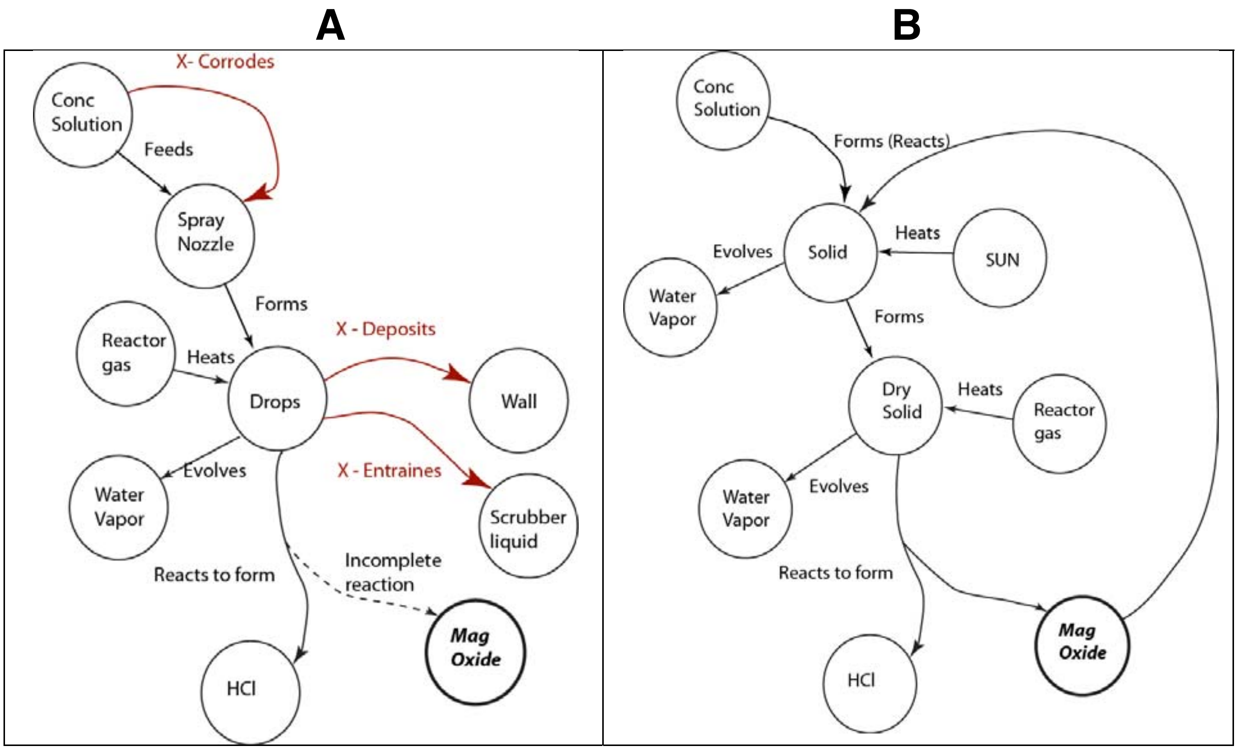

Figure 4. A- Spray process function diagram; B- MCC process function diagram

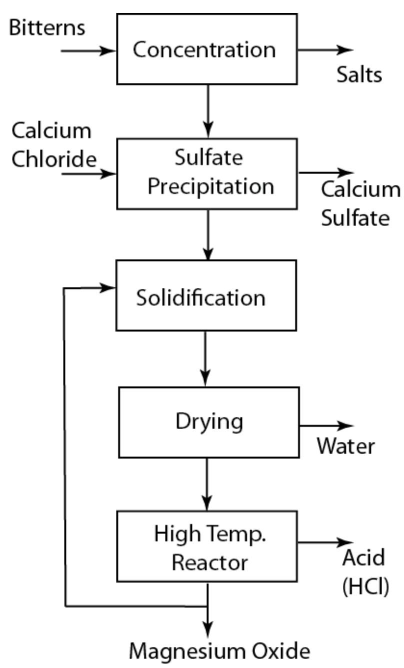

Figure 5. Modified block flow diagram

Carbon dioxide footprint (unit ratio of carbon dioxide) is the one key measure of process performance. This change in the process uses low-temperature drying to remove additional water. This is a significant advantage and is an example of applying the principle of a pre-action to reduce harm. The ideal process has no emissions of CO_2, either chemically released or from combusting fossil fuels. Solidification and drying improved ideality of the process and resulted in a simpler high temperature reactor.

Validation

Pilot scale testing was performed to quantify the effectiveness of each of the unit operations and to estimate the energy requirements. A design material and energy balance integrates this information. The pilot system was designed and built at the MCC Appropriate Technology Development Center near Bogra, Bangladesh. The process streams were analyzed to determine the anion and cation concentrations with the ion chromatograph methodology [7], which is one of the few techniques in which precise measurements of sodium, potassium, and magnesium can be determined simultaneously. The pilot unit was a study of contrasts regarding the level of sophistication, from an effective rudimentary technology to ion chromatography. The final process block flow diagram evolved from experimental insights is shown in Figure 6.

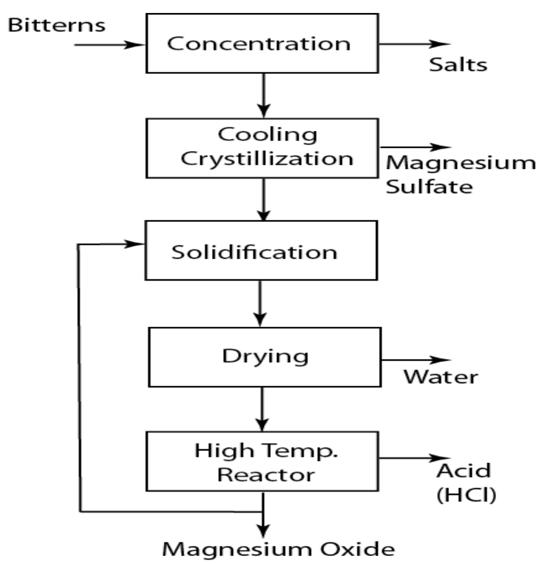

Figure 6. The MCC process block flow diagram.

Using the results of the optimized reaction condition runs, a material and energy balance was constructed with the component and elemental compositions, mass weights of materials, and energy calculations based on thermodynamics [8,9]. The results showed the energy requirement of the high temperature furnace was too high to be competitive with Portland cement. Applying the 40 principles methodology reduced the furnace energy requirement by 35%. The recovered heat was transferred to the combustion air using a regenerative heat recovery system.

Preliminary design of a commercial sized plant and cost analysis showed that the steps before the high temperature reactor are possible with solar energy[10] and the only fossil fuel required is for the high temperature reactor.

Conclusions:

The functional analyses of the magnesium oxide process focus the innovative thought process. At the heart of the improvements, which resulted in the MCC process, was the application of the ARIZ type methods.

Although the process appears much more complex than the Aman process, it has tremendous advantages. The process uses solar energy for most energy needs. The solar collection systems have been optimized to maximize performance and minimize the collector area. An intermediate process stream concentrated in magnesium can be easily stored and transported.

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