DEVELOPMENT AND CHARACTERISATION OF SLAKED LIME GRANULES FOR CHEMISORPTION IN DESULPHURISATION REACTORS

Recently imposed limitations of sulphur emission of marine vessels have increased the interest in development of efficient solutions for sulphur removal from flue gases. Chemisorption reactors (dry scrubbers) with slaked lime granules have the advantage that they do not produce liquid waste which is expensive to treat on the vessels. Slaked lime granules remain solid and the spent granules can be unloaded at ports and used for other purposes. Besides, the reaction can be carried out in compact reactors.

Performance of such granules is a multidimensional issue. However, it becomes necessary to find methods to characterise the granules for comparing granules of different suppliers, different sizes, different porosities, different prices, etc. so that their performance and economics in full scale applications can be guaranteed.

In case of chemisorption of sulphur dioxide by slaked lime granules, it is highly desirable that they have a large chemisorption capacity, and that the rate of chemisorption is fast enough. Chemisorption capacity at infinite time is one important theoretical measure, but for industrial purposes, more realistic measures are needed. Similarly, the initial chemisorption rate is not a sufficient measure of how fast the uptake of sulphur dioxide is.

In this work, experiments were carried out with a variety of granules of different sizes with different incoming sulphur dioxide concentrations at different temperatures with a pilot scale reactor, and a few practical performance measures of chemisorption capacity and rate, including breakthrough time, were calculated from the experimental results. Nonlinear models were then developed for predicting those measures.

The tests also relate the granulation process variables with the performance characteristics of slaked lime granules from experimental data.

Introduction

Desulphurisation is a necessary environmental protection measure in several industries including power generation and mineral processing. It has recently been in the limelight because of a new European commission directive 2005/33/EC, which essentially states that sulphur content of the flue gas from marine vessels in sulphur emission control areas (most of northern parts of Europe) must not exceed a limit corresponding to 0.1% sulphur content in the fuel starting from 1 January 2015. Shipping lines can either use more expensive fuel with low sulphur content or install desulphurisation equipment on board.

There are several desulphurisation processes in use in industries, including wet, semi-wet, semi-dry and dry processes, which generally make sulphur oxides react with slaked lime or in rare cases, caustic soda. The wet processes tend to have a higher efficiency, but also have higher pressure drops and energy consumption. Besides, they produce liquid effluent which cannot be discharged into the seas untreated. Wet scrubbers, including semi-dry and semi-wet reactors are still the most commonly used equipment. Dry processes have the benefit of producing solid waste which is easy to store on the ship and unload on ports. The chemisorption process can be carried out in fairly compact fixed bed column reactors like the one developed in Nordkalk. It has several benefits, and can be the preferred equipment in future if efficient granules are available, and if there is sufficient deep knowledge about the operation of the reactor so that maximum mileage is derived from limited space.

Nonlinear modelling

There is hardly any process or material behaviour which is absolutely linear. It is therefore wise to treat the nonlinearities rather than ignore them. The proponents of linear techniques draw on their simplicity and the possibility of adding nonlinear terms in linear regression. Often this is not done, and is not efficient even if it is done. Nature does not follow the simplicities that we try to fit it in, using common linear techniques.

Nonlinear modelling can be carried out with a variety of methods. The older methods include linear regression with nonlinear terms, polynomial regression and nonlinear regression. These have several limitations. The newer methods include feed-forward neural networks, kernel regression, multivariate splines, etc. which do not require a priori knowledge of the nonlinearities in the relations.

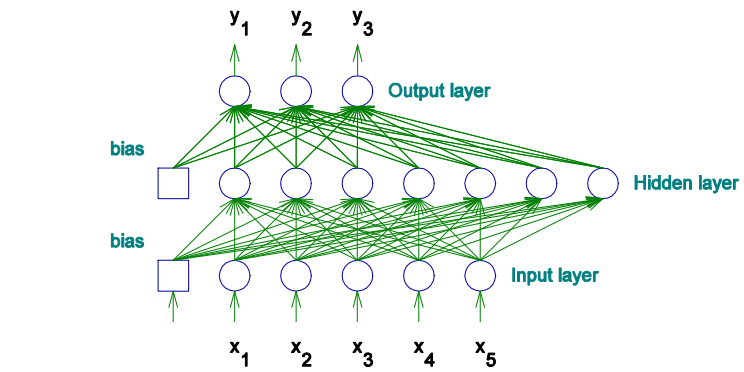

Figure 1. A typical feed-forward neural network

Feed-forward neural networks have the so-called universal approximation capability [1] which make them particularly suitable for most function approximation tasks we come across in engineering. The user does not need to know the type and severity of nonlinearities while developing the models. In other words, we have free-form nonlinearities in feed-forward neural network models.

Feed-forward neural networks resemble structurally and to a smaller extent functionally the networks of neurons in biological systems. Like the networks of neurons in the brains, artificial neural networks also consist of neurons in layers directionally connected to others in the adjacent layers (see Figure 1).

There are many different types of neural networks, and some of them have practical uses in process industries [2]. Neural networks have been in use in process industries for about twenty years [3]. The multilayer perceptron, a kind of a feed-forward neural network, is the most common one. Most neural network applications in industries are based on them [4 - 9].

In a feed-forward neural network of the kind shown in Figure 1, the output of each neuron i in the feed-forward neural network is usually given by

$$z_i = \sigma\left(\sum_{j=0}^{N} w_{ij} x_j\right)$$

where σ is called the activation function, and is usually the logistic sigmoid, given by

$$\sigma(a) = \frac{1}{1+e^{-a}}$$

The incoming signals to the neuron are x_j, and w_{ij} are the weights for each connection from the incoming signals to the i^{th} neuron. The w_{i0} terms are called biases. This results in a set of algebraic equations which relate the input variables to the output variables. Thus, for each observation (a set of input and output variables), the outputs can be predicted from these equations based on a given set of weights. The training procedure aims at determining the weights which result in the smallest sum of squares of prediction errors.

There are a variety of training methods in use today. Back-propagation used to be the most common training method very many years back. Today, most people use good optimisation methods [10] instead.

Granulation experiments

The granulation process is fairly simple. Slaked lime in powder form is first added in a mixer with a vertical axis of rotation. Water is added uniformly over a period of 1 minute while the mixer is rotating. The mixer is allowed to rotate for different periods of time. The granules are then dried before they are sent for testing or use.

Several variables affect the outcome of granulation. The most important variable is the amount of water, followed by the temperature of water and the temperature of lime. Mixing

time also matters, and so do other variables including rotational speed of the mixer.

In the first stage of granule development work, only 11 experiments were carried out with the aim of developing very rough preliminary models for the properties of the granules. Among the properties of the granules, the surface area was of prime interest, but other properties like granule size, compressive strength, chemisorption capacity and selectivity were also followed from some of the experiments. Surface area varied between 16.4 m^2/g and 25.5 m^2/g in those experiments, with an average of 21.3 m^2/g.

Nonlinear model of granulation

From the 11 experiments, very rough, preliminary nonlinear models were developed for some of the properties of the granules. The property which was of most interest at that time was the surface area as measured by the BET method.

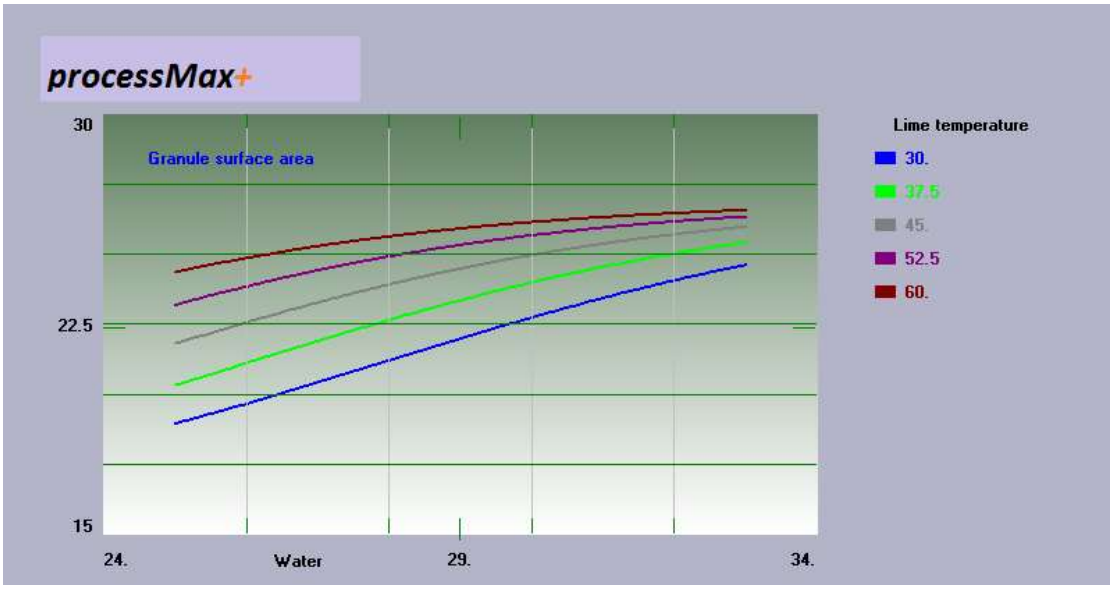

Figure 2. Surface area as a function of the amount of water for different lime temperatures

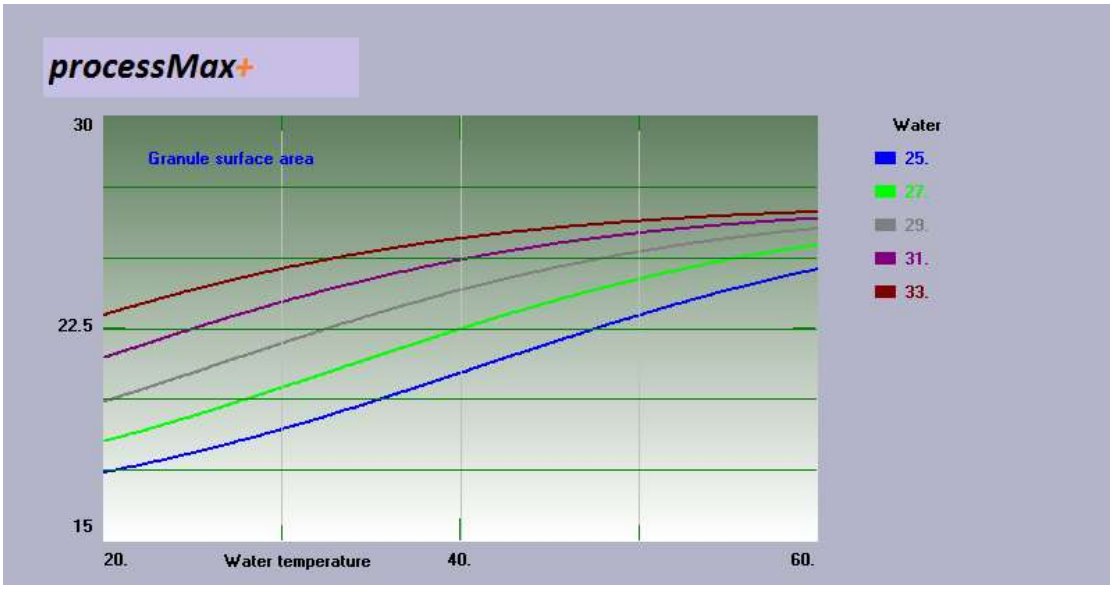

Figure 3. Surface area as a function of water temperature for different amounts of water

Nonlinear models in the form of feed-forward neural networks with one hidden layer were attempted with various configurations using the NLS 020 software. One or more of the weights of the models were restricted in many of the runs. The selected model was implemented in a PROCESSMAX+ system, a set of software components for facile use of nonlinear models. This nonlinear model never predicts negative values of surface area.

Amount of water, water temperature as well as lime temperature showed strong positive effects on the surface area. The curves tend to flatten at higher values of each of these variables, implying that higher and higher surface areas cannot be achieved by just increasing those variables.

Figure 2 shows plots of surface area as a function of the amount of water for five different values of lime temperatures, keeping other input variables constant. Figure 3 shows plots of surface area as a function of water temperature for different amounts of water.

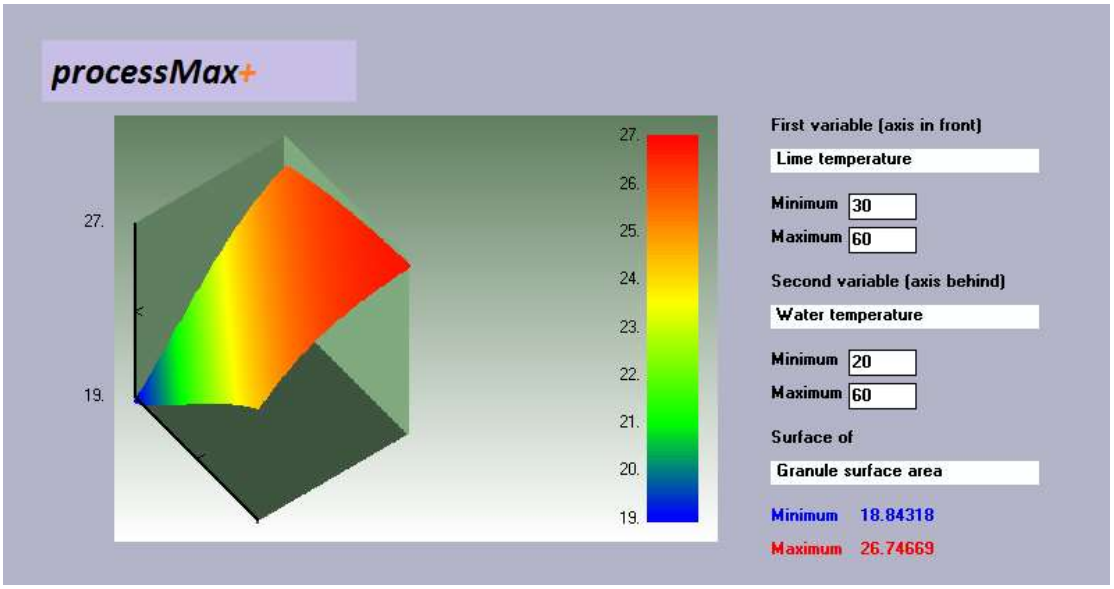

Figure 4. Surface area as a function of lime temperature and water temperature

Figure 4 shows a three-dimensional surface plot of surface area as a function of lime temperature and water temperature. All these plots indicate positive effects of these three important variables, and that a limit is reached if these variables are increased.

These are preliminary results. More experiments are planned for this work which will include more extensive experimentation followed by development of nonlinear models which will help us decide the best conditions for producing the granules on a large scale.

Reactor experiments

A fixed bed chemisorption reactor was constructed in 2014 to demonstrate the complete solution for flue gas desulphurisation on marine vessels. The granules are loaded upto a certain height for these experiments, but on a ship, they are fed more or less continuously by rotary feeder, and the spent granules are removed from the bottom also by another rotary feeder. The flue gas is generated by an engine burning fuel oils with different amounts of sulphur. The flue gas thus contains mostly carbon dioxide and steam with some amounts of sulphur oxides, mainly sulphur dioxide. There is a facility to further increase the temperature of the flue gases to some extent. After the exit sulphur dioxide concentration of 20 ppm is reached, the flow is stopped and the reactor is allowed to cool down. Spent granule samples are taken from different heights in the reactor for analysis of their sulphur and carbonate contents.

Sulphur dioxide in the exit gas is the main consequence of the process which has to be controlled. It depends on a lot of variables including sulphur dioxide concentration in the incoming gas, flow rate, temperature of the incoming gas, temperature of the granules, size distribution of the granules, height of the column of granules, surface area of the granules, etc.

Experimental data from a total of 25 experiments was available for developing nonlinear models. These experiments are not systematic or planned but in future when more experiments will be carried out, they will be planned. Several variables were followed as consequences of operating the reactor. One important variable for characterising the granules is breakthrough time for 20 ppm sulphur dioxide exiting the reactor. This variable varied from 4 hours to 80 hours, with an average of 17.5 hours.

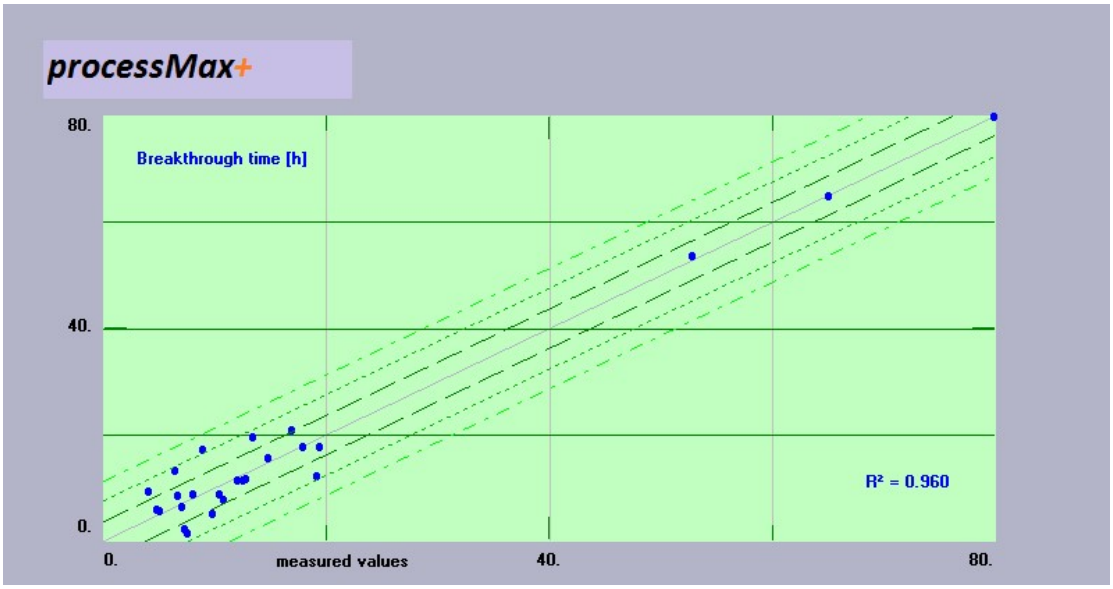

Figure 5. A plot of experienced breakthrough time against the breakthrough time predicted by the nonlinear model

Nonlinear model of the reactor

A large number of nonlinear models in the form of feed-forward neural networks with one hidden layer with sigmoidal activation functions were attempted with different configurations using NLS 020 software. One or more weights of the models were restricted. From the 25 experiments, preliminary nonlinear models were developed for breakthrough time and some other consequences of the process. Here, we report only the nonlinear model for breakthrough time, which is of most interest as a granule characterising variable.

Figure 5 shows a plot of experienced breakthrough time against the breakthrough time predicted by the nonlinear model. It has a rms error of 3.79 hours, which amounts to a correlation coefficient of 95.97%. The maximum absolute error of the model on this data was 8.47 hours. Although the correlation coefficient is quite high, the maximum error is also fairly large. It seems there is still a good scope for improvement of this model, and more input variables are probably desirable.

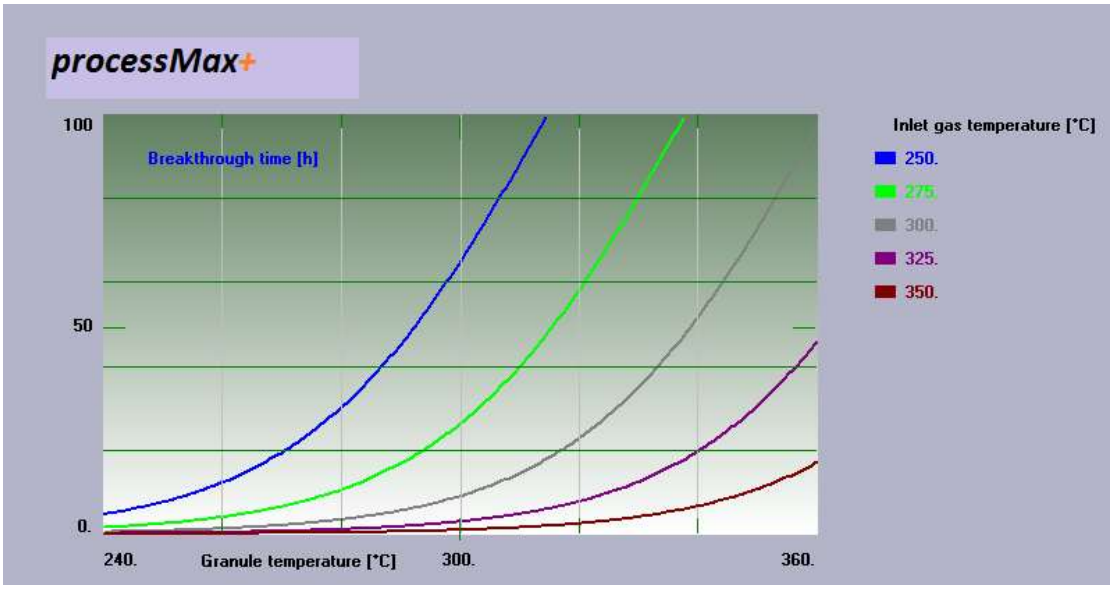

Figure 6. Effect of granule temperature on breakthrough time for different inlet flue gas temperatures

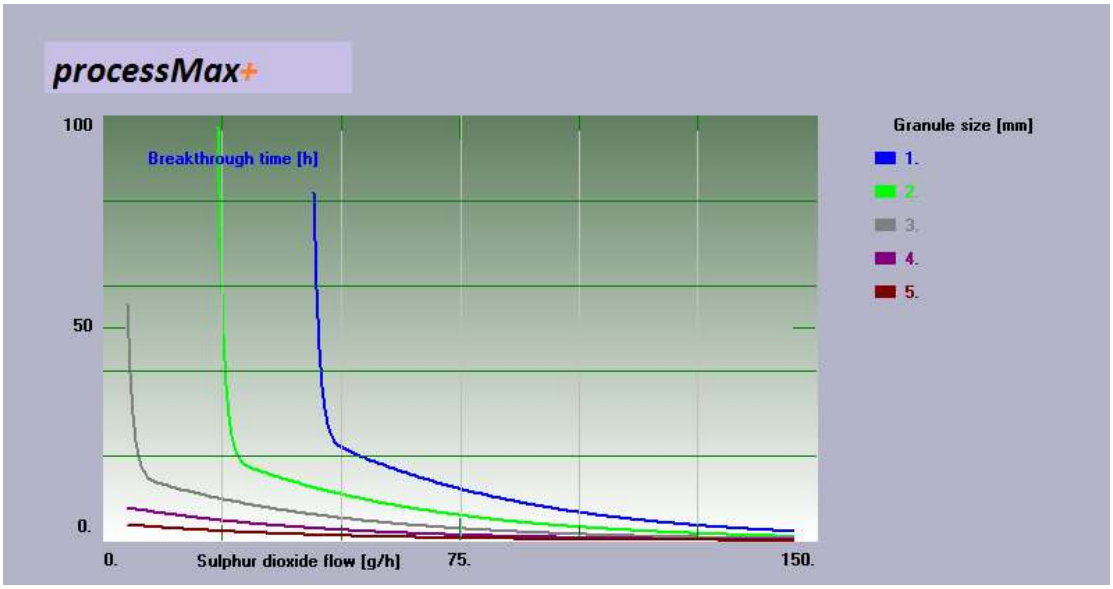

Figure 7. Effect of sulphur dioxide flow rate on breakthrough time for different granule sizes

The selected model was implemented in a processMax+ system for use and analysis of the nonlinear model. This nonlinear model never predicts negative values of surface area, but predicts zero as the asymptotic minimum breakthrough time if the sulphur dioxide concentration or flow rate are infinite.

Sulphur dioxide flow rate, granule temperature as well as flue gas temperature showed strong effects on the breakthrough time. The effect of granule size is also significant, according to this model. Figure 6 shows the effect of granule temperature on breakthrough time for different inlet flue gas temperatures as predicted by the nonlinear model. Higher granule temperatures result in exponentially longer breakthrough times while lower inlet flue gas temperature results in higher breakthrough times.

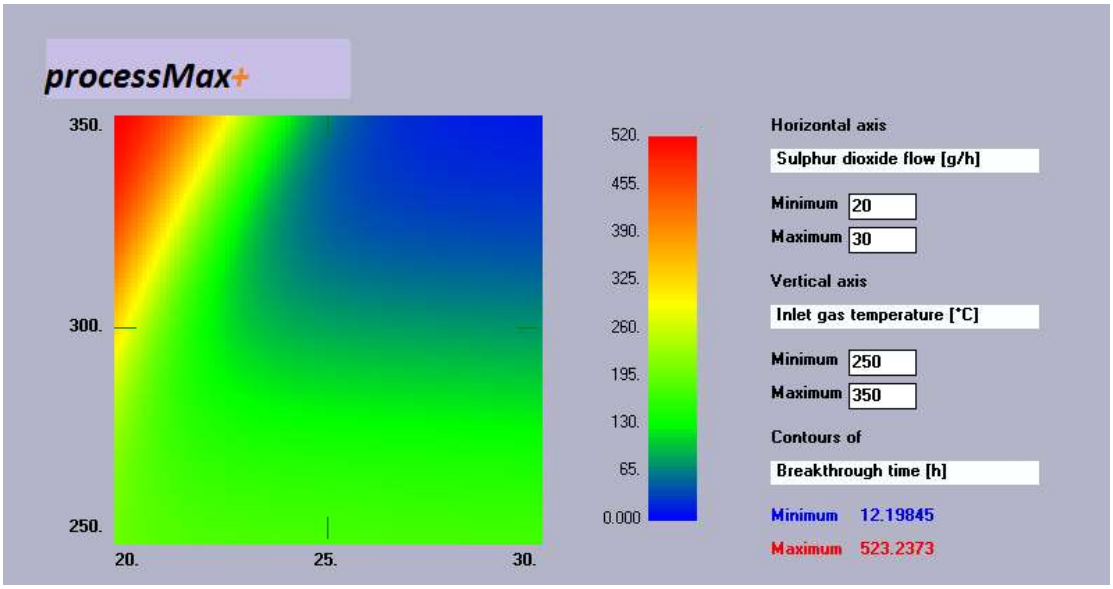

Figure 8. Contours of breakthrough time plotted on a plane of sulphur dioxide flow rate and inlet flue gas temperature

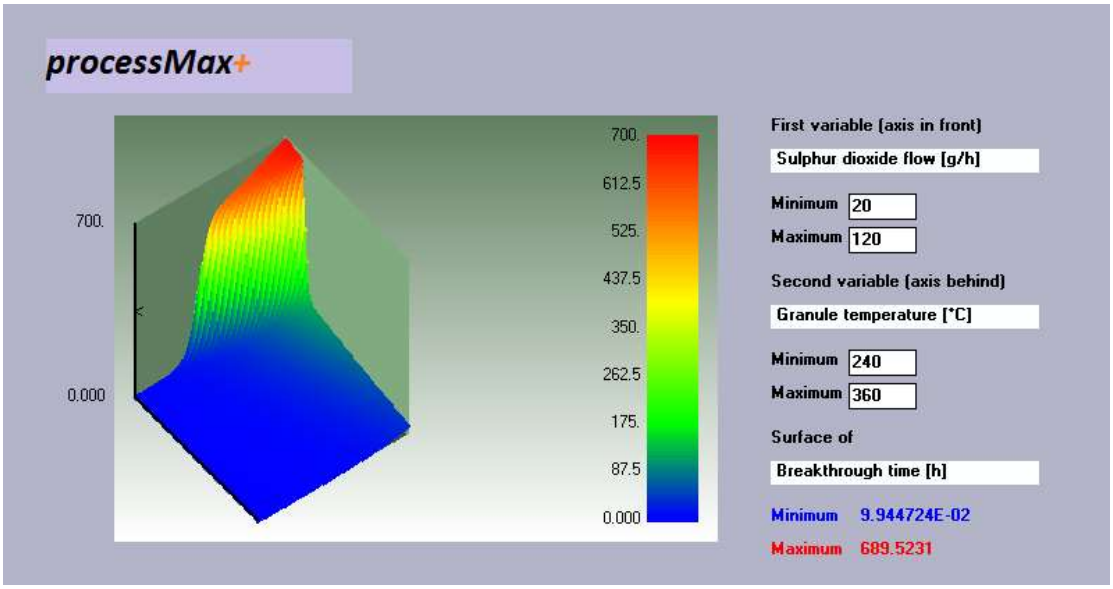

Figure 9. Surface plot of breakthrough time against sulphur dioxide flow rate and granule temperature

Figure 7 shows the effect of sulphur dioxide flow rate on breakthrough time for different average granule sizes as predicted by the nonlinear model. There is a sharp bend in the effect of sulphur dioxide flow rate, and the location of that bend depends on other input variables. Lower sulphur dioxide flow rates result in much larger breakthrough times.

Figure 8 shows contours of breakthrough time plotted on a plane of sulphur dioxide flow rate and inlet flue gas temperature. From Figure 6, we saw that increasing inlet flue gas temperature reduces the breakthrough time if other input variables are kept constant. However for very low sulphur dioxide flow rates, the effect can be opposite as seen from Figure 8. This has not yet been confirmed with specific experiments.

Figure 9 shows a three-dimensional surface plot of breakthrough time against sulphur dioxide flow rate and granule temperature. Low sulphur dioxide flow rate and high granule temperatures result in very large breakthrough times. This too needs to be confirmed with experiments in such a range.

Conclusions

Granulation is the key to the dry sulphur dioxide removal process from flue gases. Well-optimised granulation would result in high chemisorption capacity and faster chemisorption, making it a clearly better alternative to the wet processes which are in common use today. This work shows some early results of granulation process development and granule product development. Nonlinear modelling has helped us speed up this work significantly, and in future, more experiments will be carried out, allowing us to develop better nonlinear models of granulation, and calculate the conditions for producing granules with desired characteristics.

The granules need to be used in the dry scrubbing process efficiently. Early experiments have allowed us gain a fair amount of knowledge of the behaviour of granules in the process. Nonlinear models have been developed for breakthrough time and some other consequences of the process, which allow us to calculate good operating conditions.