The sulphuric acid market has been experiencing severe supply instability in several parts of the world over the past year. This is due to a host of market forces, foremost among them being the reduced supply of smelter acid due to the shutdown of several smelters, at the same time that phosphate fertilizer plants, the largest users of sulphuric acid, are experiencing high operating rates.

The situation is further exacerbated by sporadic sulphur shortages, price increases of this key raw material, and increased sulphur demand from China for fertilizer production. The net effect is an increase in the price of merchant acid and increased interest in boosting sulphuric acid production rates for merchant or captive use.

Oxygen enrichment has been used by many industries to economically increase the capacity of air-based processes. Traditional applications include sulphur recovery, fluidised catalytic cracking and sulphuric acid regeneration.

Oxygen enrichment is routinely practiced to provide additional capacity without the expense of a new unit or a major facility upgrade. There is increasing interest in the use of oxygen enrichment to upgrade virgin sulphuric acid production.

The addition of oxygen enrichment to a sulphuric acid plant can significantly enhance overall profitability when merchant prices are high.

### Oxygen enrichment for sulphuric acid manufacture

Oxygen enrichment may be considered for sulphuric acid plants, on either a short-term or long-term basis. Reasons include:

- **Cost reduction through displacement of merchant acid consumption.** Where acid requirements exceed on-site acid production and merchant acid prices are high, oxygen enrichment can be used to reduce overall operating costs.
- **Cost reduction through shutting down production capacity.** Where multiple sulphuric acid plant trains are in operation, it may prove to be economical to shutdown one train and boost remaining production through oxygen enrichment.
- **Profit enhancement through incremental acid production.** Where acid can be exported to the merchant market and prices are high, it may be attractive to boost acid production through oxygen enrichment and increase export.
- **Profit enhancement through incremental final product.** Where sulphuric acid is used in the production of another product, oxygen enrichment can boost final product rates when merchant acid supplies are tight.

A highly simplified process flow diagram for a typical sulphur burning sulphuric acid plant is shown in

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**Fig. 1:** Simple process flow diagram of double adsorption sulphuric acid plant
Figure 1. Molten sulphur and excess dry air are introduced to the furnace where sulphur dioxide is produced. Heat from the exothermic process is removed in the waste heat boiler and then the sulphur dioxide is reacted with the remaining oxygen in a four or five pass converter to make sulphur trioxide. The sulphur trioxide is adsorbed into sulphuric acid in two adsorption towers one between the third and fourth stage of the converter, the other after the last stage. The sulphuric acid is diluted with water to final product concentration and pumped to storage. The process generates a significant amount of waste heat that is usually used to generate steam and electricity.

**Process description: oxygen enrichment**

Typical limitations on combustion processes such as the sulphuric acid process are the amount of available combustion air or process equipment hydraulic limits. When these limits are reached, there are several options that can be considered, if additional capacity is required:

- **Build a new plant.** This is usually the most expensive option and is only considered when all other options have been eliminated and the desired increase in capacity is sufficient to justify the expenditure.

- **Replace the air blower with larger capacity equipment.** This approach typically requires significant capital investment, since there will often need to be additional plant modifications made to accommodate the additional volume of gas to be processed and heat generated. Often pressure drop limitations make this option more expensive than it might first appear.

- **Add a supplemental blower.** This option is similar to blower replacement, but potentially lower cost. One problem with this approach is that as extra air is added, backpressure increases and the capacity of the main blower is reduced, so full benefits are not realised.

- **Add oxygen.** This option tends to be the most economical solution for many applications. Oxygen is added to the discharge of the air blower, through a specially designed diffuser. Adding oxygen increases firing capacity without significant increase in volume of gases to be handled. The addition of oxygen may also enhance process conversions/yields depending on how it is used.

    The amount of oxygen to be added is dependent on several factors, including:
    - desired maximum production capacity;
    - furnace temperature limitations;
    - waste heat boiler limitations;
    - overall plant cooling limitations;
    - pressure drop limitations;
    - materials compatibility with elevated oxygen concentrations (the limit for conventional materials is 28% oxygen).

    Typically the amount of oxygen required to make incremental sulphuric acid is about 0.5 tonne oxygen/tonne acid. For example, to get a 5% increase in production from a 2000 t/d acid plant, about 50 t/d of oxygen is required.

    If pressure drop is limiting, such that the total volume of gas through the process needs to be held constant, this ratio increases a little, since some air will need to be backed out, in order to reduce nitrogen to the process.

    An oxygen enrichment supply system consists of a source of oxygen, a flow control skid and a diffuser to introduce oxygen into the furnace air. The flow control skid and diffuser are specially designed to ensure safe operation along with excellent control and mixing.

    Proven systems are used to provide interlocks between the plant and the oxygen supply system to avoid adverse or unsafe conditions arising within the sulphuric acid plant.
Technical considerations with oxygen enrichment

Whenever oxygen is added to a furnace, certain key operating and safety criteria need to be addressed. Combustion becomes more intense, temperatures increase, more heat is generated and reaction product concentrations can change, based on new kinetic and equilibrium conditions. For sulphuric acid production, furnace temperatures and waste heat boiler loading are of primary importance. In order to be able to predict performance with oxygen enrichment, a process simulation may be prepared and analysed, using plant data and equipment specifications as input. The simulation provides information on furnace conditions, downstream heat recovery, product conversion, product capacity and stack gas conditions. It predicts how much oxygen is required to meet incremental production and the impact on existing process equipment, along with which process limitations, if any, are encountered. Often suggestions can be made to overcome identified plant limitations. The quality of the simulation is a function of available models and thermodynamic property information, matched with practical experience from applying oxygen enrichment at customer sites. Furnace temperatures as a function of oxygen enrichment level, for a typical sulphuric acid furnace, are shown in Fig. 2.

Choice of oxygen supply mode

The correct choice of oxygen supply is critical in obtaining the best economics and is a function of several different parameters. There are four basic options to be considered.

- **Liquid oxygen (LOX).** This mode of supply is the most flexible. Oxygen is delivered as liquid by truck, from one of several central manufacturing facilities. A cryogenic LOX storage tank is installed at the site, along with a vaporiser, by the oxygen supplier. Oxygen is withdrawn from the tank and vaporised as required to meet process requirements. The tank is sized to ensure that there is always sufficient capacity to meet demand and is refilled by road tanker, as required according to on-tank volume information, communicated by telemetry to the LOX supplier. Product LOX usage and storage tank/vaporisation rental fees are invoiced monthly. The major attraction of this mode of supply is that there is minimal up front investment and little in the way of ongoing commitment. Liquid oxygen can be consumed as required, at varying flow rates, continuously or intermittently. In addition, installation can be rapid (within 1-2 months) and LOX can even be used as a temporary supply until a longer-term solution is installed. The disadvantage of LOX is that it has a higher unit price. Typically LOX is used for volumes between 0-50 t/d and/or where demand is intermittent or not projected to be long term. See Fig. 3 for a typical installation.

- **Oxygen vacuum swing adsorber (VSA).** This mode of supply provides economical oxygen by on-site generation. The process separates out oxygen from the feed air by adsorption and subsequent desorption of nitrogen, moisture and carbon dioxide under vacuum. The oxygen typically has a concentration of around 90 to 95% and is compressed to the desired process requirement. To provide an uninterruptible supply, a backup LOX tank is typically included in the supply configuration. Vacuum swing adsorbers can either be purchased or a long-term supply agreement with the supplier estab-
Oxygen enrichment

The following economic feasibility assessment for expansion of sulphuric acid production is based on generic published data, using typical industry oxygen prices of $85/t (35 c/100 scf) for LOX and $36/t (15 c/100 scf) for VSA Oxygen. Actual costs for oxygen will be site specific and are a function of volume, distance from liquid plant (for LOX) and cost of power (for on-site production).

Calculations are based on the following assumptions:

- The customer wishes to expand production of sulphuric acid. Capacity is currently limited and some merchant sulphuric acid is being purchased from external sources at an average $55/t.
- For incremental production, only variable costs are to be considered.
- It is assumed that there is no additional capital investment and that all other costs (such as maintenance and overheads) are fixed.
- For incremental sulphuric acid production, it is assumed that credit can be taken for incremental steam and electricity production. The credit with oxygen is assumed to be the same as for air. In practice it may be slightly better due to enhanced heat recovery due to elevated furnace temperatures. Four cases are analysed: base case (air-based production); base case (merchant); oxygen enrichment using LOX; oxygen enrichment using VSA Oxygen. Results of the analysis are given in Table 1.

Conclusions from economic assessment

Usually, the most economical method for producing acid is to load up existing sulphuric acid production to maximum capacity. Once this limit is reached, the choice is between purchasing merchant acid and upgrading the plant through oxygen enrichment or other route. An exception might be where multiple units are currently being operated and there is an opportunity to shut one unit down, by implementing oxygen enrichment on the other units.

Both LOX and VSA supply modes can provide incremental sulphuric acid at prices that are competitive with typical merchant prices. For LOX, the breakeven point is around $40-45/t acid. For VSA, the breakeven point is around $20-25/t. Using Oxygen can enhance profitability of incremental production significantly, when merchant sulphuric acid prices are high.

Using Oxygen need not require a long-term commitment to be justified. If there are short term concerns regarding the availability or price of merchant sulphuric acid, oxygen should be considered even if only used on a temporary basis (for temporary use, LOX is usually preferred for best overall economics.

For a 2,000 t/d sulphuric acid plant, producing an incremental 5% capacity using oxygen can result in annual savings in the range $350,000 to $1,300,000, depending on merchant acid prices and chosen mode of supply for oxygen.

Production of additional downstream products, such as phosphoric acid, with this additional sulphuric acid can significantly add to plant profitability.

Project execution

A staged approach to introducing oxygen enrichment is recommended, since there are a number of issues that need to be adequately addressed if oxygen enrichment is going to be commercially and technically successful.
phuric acid plant may be prepared process. A process model of the sul-
impact of oxygen addition to the
It is important to understand the
Technical feasibility

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<th>Variable costs:</th>
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<th>Consumption/ lb acid</th>
<th>Base case with no capacity limit $/t acid</th>
<th>Base case with merchant acid $/t acid</th>
<th>O2 with LOX $/t acid</th>
<th>O2 with VSA $/t acid</th>
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Table 1: Overall variable cost economics for incremental sulphuric production using oxygen enrichment

Generic costs from SRI Consulting PEP yearbook 2000. O2 prices are typical industry values.

Economic feasibility
The first step is to perform a preliminary economic assessment to determine whether the addition of Oxygen is going to be economically attractive when compared to alternatives. The customer and industrial gas supplier work together, to determine the best options for upgrading the plant. For oxygen enrichment, a key issue is the mode of supply. Unless a pipeline is located nearby, the choice is between LOX and an on-site oxygen generator. Factors to be taken into account include:
- Continuous vs intermittent oxygen requirement;
- The volume of oxygen required;
- Whether any co-product Nitrogen or CDA can be used at the site;
- Distance from gas suppliers liquid plant;
- Cost and availability of power;
- Level of certainty that volumes will be required for long term;
- Customer preferences to purchase generation equipment or gas.

Often an approach is taken where LOX is used initially - say first year. The customer operates the facility with oxygen enrichment and assesses its effectiveness. At the end of this initial period a decision is made either to continue using LOX or convert to an on-site.

Technical feasibility
It is important to understand the impact of oxygen addition to the process. A process model of the sulphuric acid plant may be prepared and used to determine critical process parameters such as furnace temperature, waste heat boiler performance and overall heat & material balances around the facility. This information is used to assess technical feasibility and to define critical parameters for the site trial.

Site trial
Assuming that the project looks economically attractive, the next step is usually to perform a limited period site demonstration. After safety reviews and training, a temporary LOX tank installation is placed at the site, along with a flow control skid. The oxygen diffuser is installed in the air blower discharge (this is usually hot-tapped, so no shutdown is required). The length of the trial is up to the customer, but is usually at least a week, with increasing amounts of oxygen added until the desired capacity or other limitation is reached. This is the final go / no-go point before implementation.

First year operation
Assuming that the trial is successful, the customer can immediately start using oxygen enrichment if LOX is to be used. Depending on the nature of the setup for the trial, the LOX system can be left in place or replaced with a permanent installation. If required, the industrial gas company can provide ongoing technical support to resolve any issues and enable trouble-free, efficient operation. It is recommended that audits be carried out at 6 and 12 months to review take patterns, process performance and any changes required to meet ongoing needs.

Longer term operation
As part of the ongoing relationship between customer and industrial gas supplier it is suggested that alternative supply modes be reviewed after 12 months of operation to see which option will provide the most effective and economical solution longer term. This will be based on actual usage patterns during the first year of operation and projections on future needs. Since operating conditions vary from year to year, it is recommended that ongoing reviews (typically every 6-12 months) take place between the customer and supplier. In addition, a service contract may be considered where ongoing technical support is made available to help provide safe, reliable and efficient oxygen enrichment operation.

Overall conclusions
For producers of sulphuric acid looking to increase production or reduce costs, the addition of oxygen can prove to be financially attractive and relatively straightforward to implement. It is important to work closely with an industrial gas supplier with a proven track record in oxygen enrichment, to successfully resolve the technical issues and identify the best implementation strategy and oxygen supply, based on expected use patterns, overall volumes and opportunities for integration.