

## FINAL TECHNICAL REPORT

Project: Advanced Sorbents as a Versatile Platform for Gas Separation  
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Principal Investigator: Neil Stephenson  
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## Program Background

The program objective was to develop materials and processes for industrial gas separations to reduce energy use and enable waste reduction. The approach chosen combined novel oxygen selective adsorbents and pressure swing adsorption (PSA) processes. Preliminary materials development and process simulation results indicated that oxygen selective adsorbents could provide a versatile platform for industrial gas separations. If fully successful, this new technology offered the potential for reducing the cost of producing nitrogen/oxygen co-products, high purity nitrogen, argon, and possibly oxygen. The potential energy savings for the gas separations are appreciable, but the end users are the main beneficiaries. Lowering the cost of industrial gases expands their use in applications that can employ them for reducing energy consumption and emissions.

At the program onset, there were no commercial systems that employ equilibrium-selective oxygen adsorbents for separating oxygen due predominantly to lack of suitable materials. The current program built on existing Praxair compositions developed under ATP cooperative agreement 70NANB5H1083 to move them closer to commercialization. The focus of the program was changed, with DOE consent, to pursue current oxygen selective adsorbents for gas purification as an early commercialization opportunity. Materials development was continued in parallel in an attempt to generate new materials suitable for the broader market of bulk air separation as originally targeted.

The materials development program was structured to create improved oxygen selective adsorbent compositions, to develop manufacturing capability, to demonstrate agglomeration to useful forms, and to assess hazards associated with preparation, use and disposal. Parallel activities were to identify applications, markets, and commercialization incentives.

## Program Highlights

### Task 1: Adsorbent Composition

- Established a manufacturing capability for **IA-3** and produced 20 kg of material. This material is attractive for purification applications
- Estimated adsorbent production cost and identified sources for key intermediates
- Development of a composition suitable for bulk air separation to produce nitrogen and oxygen coproducts was not successful although **IA-2** partially meets the requirements.

### Task 2: Agglomeration

- Showed that extrusion technology with polymeric binders or compaction with additives can provide **IA-3** agglomerates with useful combinations of physical and adsorption properties
- Showed that agglomeration is not a barrier to commercialization of oxygen selective adsorbents and that the associated cost represents a small fraction of the total adsorbent cost

### Task 3: Hazard Assessment

- Showed that the material designated **IA-3** meets the definition of a Division 4.1 Flammable Solid, Packing Group II
- At atmospheric pressure, **IA-3** bulk powder has a limiting oxygen concentration (LOC) value of 13% O<sub>2</sub>, meaning 13% or greater O<sub>2</sub> is necessary for combustion.
- **IA-3** dust has a limiting oxygen concentration (LOC) of 2-5% O<sub>2</sub> and requires only 5 to 10 millijoules of energy to ignite (static charge). It is ranked as a 'strong explosive' at concentrations of 250g/m<sup>3</sup> to 1250 g/m<sup>3</sup>

### Task 4: Process and Adsorber Development

- Established the technical feasibility of purifying crude nitrogen using the composition designated **IA-3**
- Showed the economic feasibility for purification of crude nitrogen exists in a narrow production window unless other factors are included such as lack of current infrastructure

### Task 5: Applications Assessment

- Updated the projected energy savings chart for the aluminum industry and increased the projected value
- Established the need for a strong business case and significant cost advantage relative to existing technologies in purification markets

## **Program Details**

### **Task 1. Adsorbent Compositions**

It was recognized from the program onset that development of materials with suitable combinations of performance, cost, and lifetime would be a key to achieving commercial success. In addition, the pressure dependence of oxygen uptake (oxygen isotherm) would determine the suitability a material for a particular application (separation or purification). The ATP program, which served as a baseline for the DOE program, resulted in the development of two families of adsorbents. The "IC" family employs "Intermolecular Assembly" where a peripheral group on the chelating ligand bound to the axial site of a neighboring metal center for control of intermolecular packing to create an active 5-coordinate deoxy site. A second family of materials designated "IA" uses peripheral groups for formation of extended arrays with 5-coordinate deoxy sites by "Intermolecular Assembly".

The best material identified for air separation under the ATP program was designated **IC-2** and it met some of the performance requirements necessary for commercial success. Over 1 kg of **IC-2** was available from the ATP program for use in exploratory agglomeration studies. In

addition, the ATP program provided compositions designated **IA-n** with  $n = 1, 2, 3$ . These materials were structurally simpler than **IC-2** and were expected to offer a cost advantage. Both **IA** and **IC** concepts define families of materials and permit further structural variation to improve material performance. The DOE program addressed improvements to **IC-2** in the early stages including more reliable synthesis methods, and the development of new compositions, particularly in the **IA-n** family.

The program focus was changed, with DOE approval, to pursue purification applications involving trace oxygen removal. These were always viewed as near-term opportunities that could provide the experience with this new class of adsorbents that would ultimately be necessary for commercial acceptance in the broader field of air separation. In addition, the adsorbent development activity was extended into the final program year, with DOE consent, in an effort to develop materials that would be suitable for the broader application of bulk separation that was initially targeted.

Material performance still remains a key to application of oxygen selective adsorbents. We believe that the development of oxygen selective adsorbent compositions that meet all the characteristics necessary for commercial success in bulk air separation is possible in the longer term. However, at this point there is no reliable procedure to predict performance and lifetime a priori.

### **IC-Family**

The procedures to prepare **IC-2** developed under the ATP program offered poor reproducibility at best. We showed that the sorption performance of substandard **IC-2** batches could be enhanced either by recrystallization or regrowth. However, it became apparent that lack of a simple procedure to prepare consistent material would pose a barrier to commercialization. In addition, communication with Sigma-Aldrich led us to conclude that our initial cost projections were severely underestimated. As soon as it became apparent that **IC-2** was not suitable for commercialization, the synthesis optimization activities were discontinued. Other examples of the **IC** concept were prepared and evaluated. For example a new composition containing peripheral pyridyl groups was prepared that was oxygen selective with a capacity of 0.8 mmol/g at 27 °C and one atmosphere oxygen. However, the rates of oxygen interactions were modest and reversibility was poor. Based on extensive efforts including a large number of new compositions, no new members of the **IC** family were identified that provided performance worthy of further investigation. The focus of the synthesis activities was switched towards the **IA-n** family.

### **IA-n Series**

A composition designated **IA-1** was first identified under the ATP program but desorption of oxygen requires extended periods under vacuum. Although it is the simplest member of the **IA-n** family and has the lowest projected cost, it is not suitable for use in cyclic processes. However, due to availability, it was used in early studies of lifetime and in the initial development of agglomeration methods.

The best composition that we have identified for use in bulk air separation is designated **IA-2**. This adsorbent is more suitable than **IA-3** (see below) for bulk air separation since the oxygen isotherm does not saturate at low oxygen partial pressures, and the material shows increased oxygen desorption rates. **IA-2** appears to meet most of the target properties, but it is unlikely that it can provide the target economics. In addition, there are unresolved issues regarding processing hazards. The oxygen uptake for **IA-2** is strongly dependent on the oxygen pretreatment, particularly the temperature, oxygen pressure, and duration. For example, exposure of **IA-2** to 10000 torr oxygen at 27 °C changes the subsequent sorption performance, with longer exposure providing higher oxygen loadings in the low-pressure region. This

pretreatment offers continuous property tuning but also creates a potential hazard due to the need for a high-pressure oxygen exposure to bring the material into its most active state.

Attempts to develop a procedure to prepare the more active form of **IA-2** directly were not successful. However, an improved activation procedure was developed using modest oxygen pressures at subambient temperatures. An added benefit is that the oxygen capacities at one atmosphere are approximately double those of previous **IA-2** samples. Extended cycling tests for **IA-2** at 27 °C resulted in a slow performance decline (12% in two months), possibly due to decay of the active phase.

The material designated **IA-3** represents the material with the best prospect for commercialization in the short-term. It offers properties that make it well suited for trace oxygen removal, and can be produced reproducibly in quantity. We believe that **IA-3** may be commercially viable for some applications and may result in acceptance of oxygen selective adsorbent technology. However, it will not offer the energy savings targets identified in our original proposal since it is not suitable for bulk air separation. The adsorbent scale up and manufacturing studies focus on **IA-3** as a typical member of the **IA-n** family and the closest composition to commercial offering.

A large number of new compositions were prepared and screened in our pursuit of materials suitable for bulk air separation. Based on TGA tests, some compositions showed oxygen selective behavior, but capacities, reversibilities, and rates were inferior to existing Praxair materials. A few notable examples are described that offer unique characteristics. An analog of **IA-3** was prepared using 1,2-diaminopropane and the potassium salt of 4-hydroxypyridine. This material represents the first example of the **IA-series** where oxygen release rates are fast. In addition, the difference in oxygen loading (dynamic capacity) between air and oxygen at one atmosphere is much higher than expected for Langmuir behavior. Unfortunately, this composition is not suitable for use in cyclic processes since the lifetime is relatively short. Based on TGA cycling studies, it is evident that both oxygen atoms from dioxygen remain in the degraded product.

## Lifetime

The initial lifetime studies were performed using **IA-1**. The projected half-life for **IA-1** based on high-precision, short-term, thermal cycling is about 400 days under the testing conditions. Storage in ambient air caused a 50% loss in activity over two days, but performance stabilized at this level. Coupled with magnetic susceptibility measurements, the data are consistent with oxidation of half the metal centers to cobalt(III). In contrast, heating **IA-1** at 85 °C under oxygen for four days resulted in complete loss of oxygen capacity, and the magnetic moment increased by 40%. This suggests that the decomposition mechanism at elevated temperature is different from that in air at room temperature. On the basis of data collected to date for **IA-1**, we propose that the ambient temperature degradation is water promoted to give cobalt(III), while at higher temperature under oxygen, degradation occurs to generate cobalt(IV). This finding was significant since it implied that reducing water content in feed could increase the lifetime of an oxygen selective adsorbent.

The oxygen selective adsorbent designated **IA-3** has the potential for broader applications than **IA-1** due to improved ease of desorption. We demonstrated that the half-life of **IA-3** under cycling conditions is sensitive to the degree of solvent removal and that it can be increased to over 400 days by more thorough activation using temperatures up to 150 °C. The effect of temperature on the lifetime of **IA-3** was examined under cycling conditions between oxygen and nitrogen. The observed half-life is 3.3 days at 60 °C and 0.49 days at 80 °C. For comparison, the projected half-life for **IA-3** at room temperature is about 2 years. This indicates very strong temperature dependence to lifetime, and emphasizes the need to operate processes involving **IA-3** at or below ambient temperature. Analytical tests were performed to establish the

origin of the performance loss for a sample of **IA-3** that had undergone cycling for approximately 6 months. Based on a combination of mass spectrometry and NMR spectra, we found no evidence of ligand-centered oxidation implying that the performance degradation is due to metal-centered oxidation.

Lifetime under conditions of use is a key performance characteristic that will dramatically change process economic projections. Therefore, a series of experiments was designed to evaluate the influence of temperature, moisture, and oxygen partial pressure on lifetime of **IA-3** under conditions that would be experienced in an adsorbent bed for a purification application. Equipment and components for the lifetime studies were provided using internal sources of funding at a cost of over \$200K. The test system was operated for more than one year and indicated that moisture in the feed is not a critical parameter. However, the lifetime of **IA-3** is very sensitive to temperature and the extent of oxygenation. As a point of reference, the projected half-life of **IA-3** is 4.77 years at 1% oxygen feed and 40 °F. The lifetime data were used as inputs to optimize process economics.

## Large Scale Production

### IA-3 Production

The development of a large-scale production capability was established using the composition **IA-3** as a typical member of the class of materials that we intend to commercialize. In addition, **IA-3** represents the composition with the best short-term commercialization prospects. In the early bench-scale activities, 120 g of activated **IA-3** was obtained in an overall yield of 82% (three-step procedure) based on ligand. The material had an oxygen loading of 6.52% (2.04 mmol/g) indicating that the sample is very pure. As a next step, the production of 1 kg of **IA-3** was completed in-house to improve synthesis procedures and to provide material for hazard testing. The optimized synthesis makes more efficient use of starting materials, reduces complexity, increases yields, and simplifies isolation procedures which all favor reduced cost. Based on the procedure provided by Praxair, Sigma-Aldrich provided a manufacturing cost estimate of \$120/lb for **IA-3**. Cost analyses for adsorbent production indicate that most of cost is attributable to raw materials.

The subcontract with Sigma-Aldrich was updated to more accurately reflect the work that needed to be performed. An order was placed for 20 kg of **IA-3** to provide material for hazard testing, agglomeration studies, and extended lifetime studies. This larger run also allowed Sigma-Aldrich to update the adsorbent cost projections for commercial scale manufacture. The work at Sigma-Aldrich included laboratory scale studies to optimize and verify the synthesis procedure provided by Praxair, followed by the full manufacturing run. The transfer of **IA-3** synthesis to Sigma-Aldrich was more challenging than originally anticipated. It was necessary to work closely with Sigma-Aldrich to resolve a performance deficit for material that they prepare on a bench scale. With additional input and one false start, Sigma-Aldrich successfully prepared and delivered a larger batch (20 kg) of **IA-3**. We are now confident that Sigma-Aldrich is capable of manufacturing **IA-3** on a large scale. The current best cost estimate for large-scale production of **IA-3** is about \$200/lb making reasonable assumptions about recycle options. However, there are uncertainties in some raw material costs and opportunities to reduce conversion costs including outsourcing early steps.

### Intermediates Production for IA-3 and IA-2

Sigma-Aldrich has indicated that there are no current producers for the diamine precursors to **IA-2** and **IA-3**. Uncertainties in cost projections for manufacturing of **IA-3** exist due to the lack of vendors for some of the critical intermediates, and uncertainties regarding economies of scale and conversion costs. Therefore, procedures were developed using commercially available raw materials. These optimized synthetic procedures for key raw

materials (diamines) were sent to Sigma-Aldrich for possible outsourcing and will offer a direct impact on product cost.

There is also a consensus that the current laboratory-scale method for producing the diamine precursor to **IA-2** is not amenable to manufacturing. Depending on the ongoing performance and process results, synthesis studies will be performed either at Praxair or at Sigma-Aldrich to develop alternative synthetic methods. This will enable the adsorbent cost estimates to be updated. The intermediates cost reduction studies were placed on hold pending business case development for commercial applications.

## **Task 2. Agglomeration**

The exploratory phase of agglomeration studies examined the potential of specific agglomeration methods to deliver performance required for practical application of oxygen selective adsorbents. Systematic studies were performed to address the balance between performance (loading, rate) and physical properties (strength, density). In addition, potential vendors for additives and equipment were identified. Based on results obtained in the first year, the range of agglomeration methods was narrowed to three - conventional processes (extrusion/pan-pelletization), compaction, and microencapsulation. During the second program year, it became apparent that it would be difficult for microencapsulation procedures to provide the densities and porosities that are necessary. Therefore, the studies shifted to the remaining options with the primary focus on extrusion.

### **Conventional Bead Forming**

The agglomeration of oxygen selective adsorbents using polymeric binders was achieved by mixing adsorbent powder with binder solution to form a paste, which is dried to obtain beads. Extrusion of dough-like mixtures of **IA-3** with 10% polymeric binder results in samples that combine good physical strength, equilibrium performance, and mass transfer rates. Polymer selection was explored, but it is evident that conventional low-cost polymers such as polyvinylacetate can fulfil our agglomeration needs.

Parametric studies were performed to optimize porosity, density, and capacity using a hand operated extruder. The best procedure uses 10% poly(phenylene oxide) as a binder and toluene as the polymer solvent. Attrition is very low based on in-house evaluation, and densities are near 0.7 cc/g. These methods were extended to larger scale processing using a benchtop extruder and a one pound of agglomerated **IA-3** was prepared for extended lifetime studies and hazard testing.

### **Compaction**

Early studies were performed using **IC-2** due to availability at the time. Demonstrated that additives such as microgranular cellulose or Acrawax C at levels from 10 to 30% allow compaction of **IC-2** without densification or affecting sorption behavior. Pellet densities at compaction forces of 500 lb are 0.7 to 0.8 g/cc. The tensile strength of **IC-2**/binder compacts increases with increasing pelletization pressure, and has values over 200 psi at pelletization pressures near 1500 psi. Mercury porosimetry of **IC-2** compacts with additives to prevent densification indicate porosities from 23% to 54% with piece densities from 0.56 g/cc to 0.76 g/cc depending on the compaction force.

As **IA-3** became available and the future of **IC-2** became unclear, a transition was made to compaction of **IA-3**. We found that procedures that were successful for **IC-2** did not provide useful compacts for **IA-3**. Therefore, a transition was made to polymeric binders. Tablets of **IA-3** prepared using compaction methods with polymeric binders show that the majority of capacity is retained to 6000 lb compaction force. Increasing the compaction force from 200 to 4000 lbF

lowers the oxygen uptake rate by about 15% even though the equilibrium capacity is unaffected. We have also demonstrated that additives such as nylon or rayon fibers can dramatically increase the strength of compacts produced at an equivalent force. Indeed, compression and deformation occurred rather than breakage.

### Comparison of Agglomeration Methods

The properties of agglomerated **IA-3** samples produced by different methods are compared in Table 1. Note that the effective particle size is substantially larger for the agglomerates produced by compaction, and that some capacity variations reflect the quality of the initial **IA-3** powder that was used. Extrusion appears to give the best combinations of capacity, rate, density, and crush strength.

Method	Composition	O <sub>2</sub> uptake (mmol/g)	Ads rate (mmol/g/s)	Des rate (μmol/g/s)	Piece density (g/cc)	Median pore diameter (μm)	Crush strength (lbF)
Extrusion/evaporation	10%PPO	1.74	0.15	1.83	0.76	0.31	21
Extrusion/evaporation	10% PPO	1.75	0.15	1.78	0.70	0.35	12
Extrusion/evaporation	5%PPO	1.83	0.20	2.20	0.69	0.41	11
Extrusion/quench	5%PPO, Hexane	1.88	0.13	-	0.53	0.42	Deforms
Extrusion/evaporation	5%PPO, evap	1.87	0.13	-	0.62	0.39	-
Compaction (control)	10%PPO, powder	1.12	0.138	1.45	-	-	-
Compaction	10%PPO, 2000lbF, 3 min	1.13	0.047	0.74	1.05	-	24.25

### Dusting

Hazard testing results indicate that the hazards associated with **IA-3** dust clouds are substantially greater than for **IA-3** powder. Therefore, a test was developed to assess the attrition of **IA-3** agglomerates. This test involves shaking a group of agglomerate pieces in a glass vessel for several days. Preliminary tests showed that all **IC-2** compacts disintegrated within 15 minutes, and additives play only a modest role. In contrast, attrition tests for **IC-2** and **IA-3** extrudates containing polymeric binders showed minimal degradation. The fragments tended to be large enough that formation of a dust cloud would be unlikely. We believe that appropriate combination of binder, composition, and processing can provide materials that do not form hazardous dusts.

### Projected Cost and Commercial Agglomeration

Based on communications with equipment vendors and toll manufacturers, we have established that the costs of the more expensive agglomeration options are below \$5/lb, even allowing for atmosphere control. As such, the cost of agglomeration is likely to represent <5% of the total adsorbent cost.

Preliminary studies were performed in-house using extrusion on a scale closer to commercial production to allow us to optimize adsorbent performance, particularly capacity, mass transfer, and attrition resistance. Some difficulties were experienced getting the paste consistency adequate for extrusion and maintaining physical properties. This activity was discontinued since it is not viewed as a barrier to commercialization, and the problems are best resolved by manufacturers who specialize in extrusion.

### **Task 3. Hazard Assessment**

Hazard testing was conducted for the full range of oxygen selective materials both in-house and using external agencies. Initial tests were performed using **IC-2**, but a transition was made towards the **IA-series** as they became available in quantity and when it became apparent that **IC-2** was not likely to play in a commercial sense.

Standard ASTM heat of combustion testing (ASTM D4809) of **IC-2** powder yielded a heat of combustion of 5,125 cal/gm. Standard ASTM autogenous ignition temperature (AIT) testing (ASTM G72) for **IC-2** powder in 1,500 psig oxygen showed spontaneous autoignition at 115°C with a violent energy release. This AIT of 115°C is quite low compared to many non-metallic materials such as activated carbon (AIT 285°C to 355°C) or hydrocarbon oils (AIT from 170°C to 225°C). However, it should be noted that the ASTM AIT test was primarily established to qualify materials for oxygen service and does not necessarily relate to the operating conditions that we intend to use. The AIT test results do not bar us from using this or related materials with oxygen, it alerts us to the need for further testing.

A series of tests were completed for **IA-3** powder in air. The test results relating to the U.N. Transport of Dangerous Goods indicate that **IA-3** meets the definition of a Division 4.1 Flammable solid, Packing group II. Dust cloud explosion minimum energy tests for **IA-3** powder in air indicate that it is highly sensitive to ignition. Tests also indicate that the powder has an intermediate chargeability in contact with stainless steel surfaces. Under one atmosphere of oxygen, the weight loss and exotherms attributable to combustion occur at temperatures above 190 °C.

Based on the test results for **IA-3**, it is apparent that purification applications represent a lower risk than bulk air separation in view of the oxygen partial pressures involved. This is supported by preliminary TGA tests under oxygen enriched environments. Additional tests were performed to examine the limiting oxygen concentration (LOC) which is the minimum concentration of oxygen necessary to support combustion. This test helps to define the conditions that are necessary for safe use and storage. At atmospheric pressure, **IA-3** bulk powder has an LOC value of 13% O<sub>2</sub> indicating that the material will burn in air. At elevated pressures up to 400 psig, the LOC for **IA-3** bulk powder is 9% O<sub>2</sub>. The recommended maximum storage or process temperature for **IA-3** bulk powder in oxygen purities at or above the LOC is 60 °C (140 °F). The first onset of adiabatic self-heating is 85 °C (185 °F).

The LOC tests for **IA-3** dust clouds were dramatically different. **IA-3** dust has a limiting oxygen concentration (LOC) of 2-5% O<sub>2</sub> and requires only 5 to 10 millijoules of energy to ignite (static charge). In addition, **IA-3** dust autoignites at a temperature of 340-360 °C (644-680 °F). **IA-3** dust is ranked as a 'strong explosive' at or above its LOC (2-5% O<sub>2</sub>) and with dust concentrations of 250 g/m<sup>3</sup> to 1250 g/m<sup>3</sup>. At dust concentrations from 125 g/m<sup>3</sup> and 1500 g/m<sup>3</sup> the rating dropped to a 'weak explosive'.

It is evident that **IA-3** dusts are potentially more hazardous than bulk powder. It is therefore important to control, minimize, or eliminate dusting from occurring. Methods to mitigate combustion or control dusting are critical, and agglomeration to reduce dusting as measured in attrition tests is critical.

### **Pre-Manufacturing Notification**

Established that Sigma-Aldrich is willing to process the Pre-Manufacturing Notification paperwork for the three intermediates that are isolated in the synthesis of **IA-3**. They have recommended using a "low volume exemption" category that will simplify the process. However, this activity is not considered time critical in the route to commercialization.



**Task 4. Process and Adsorber Development**

Laboratory tests were designed to support the process development activity, particularly in view of the apparent slow desorption rate. A lab-scale 2-bed system was assembled and tests indicated that a vacuum/purge combination can reduce the volumes of purge gas that are necessary for regeneration. In addition, packed bed tests for purification of crude nitrogen indicated that **IA-3** could remove oxygen to ppb levels.

Process analysis of bulk air separation was performed using preliminary data for **IA-2**. This analysis indicated that the production of co-product nitrogen and oxygen from air is technically feasible. The adsorbent properties used for this work were based on adsorption properties of a real adsorbent but assumed a long lifetime. Parametric studies indicate that improvements in desorption rate would have the greatest benefit.

**Task 5. Applications Assessment****Bulk Air Separation**

The projected energy savings that can be achieved by using Oxygen Selective PSA for high yield aluminum melting was miscalculated in the original proposal. Table 1 from the original proposal has been revised and simplified to reflect this correction and is presented below. Our current estimate of the incremental energy savings for this technology is  $3.13\text{E}+12$  Btu/yr relative to current oxygen/fuel technology. This represents a 50% increase over the original energy savings estimate of  $2.03\text{E}+12$  Btu/yr stated in the proposal.

The total requirement for the high yield aluminum market is projected to be approximately 3,000 ton/day (TPD) of oxygen and 2,000 TPD of nitrogen. According to our current projections roughly one-third of this requirement, or 1,000 TPD of oxygen and 600 TPD of nitrogen, could be produced by an Oxygen Selective PSA  $\text{O}_2/\text{N}_2$  co-product plant. Acceptable product purities for high yield aluminum melting range from 50 to 90% for oxygen and from 99.9% to 99.999% for nitrogen.

**Table 1. Projected Energy Savings for the Aluminum Industry**

	<b>Current Air/Fuel</b>	<b>Current Oxygen/Fuel</b>	<b>Oxygen Selective PSA</b>
Total Al. Market - lb/yr	2.20E+10	2.20E+10	2.20E+10
Market Penetration	100%	35%	25%
Technology Fit	100%	100%	75%
Portion of Al. Market Accessible to New Technology - lb/yr	0	7.70E+09	4.13E+09
<b>Aluminum Melting</b>			
Specific Energy Use - Btu/lb	1,700	1,700	1,700
Fuel Reduction	0%	35%	35%
Direct Energy Savings - Btu/yr for Aluminum Melting		4.58E+12	2.45E+12
<b>Added Metal Reduction Energy</b>			
Metal Loss on Melting	1.50%	0.30%	0.30%
Specific Reduction Energy - Btu/lb	30,000	30,000	30,000
Energy Savings - Btu/yr for Metal Reduction		2.77E+12	1.49E+12
<b>Remelting of Dross</b>			
Dross Generation	3.00%	0.60%	0.60%
Specific Energy to Remelt - Btu/lb	2,200	2,200	2,200
Energy Savings - Btu/yr for Remelting of Dross		4.07E+11	2.18E+11
<b>Total Incremental Energy Savings - Btu/yr for High Yield Melting Application</b>		7.76E+12	4.16E+12
<b>Oxygen/Nitrogen Production Costs</b>			
Specific Oxygen Required - NCF/lb Al	NA	2.2	2.2
Total Oxygen - NCF/yr	NA	1.69E+10	9.08E+09
Total Oxygen - ton/day	NA	1,921	1,029
Specific Electric Power Consumption - kw/TPD	NA	14.9	11
Total Electric Power Consumption - kwhr/yr	NA	2.51E+08	9.92E+07
Thermal to Electric Efficiency	NA	33%	33%
Total Energy to Produce Oxygen - Btu/yr	NA	2.59E+12	1.03E+12
<b>Net Incremental Energy Savings - Btu/yr for High Yield Melting Application</b>		5.17E+12	3.13E+12

Additional marketing studies have provided preliminary projections for the market size and product requirements of other potential markets for oxygen-nitrogen co-products. The glass industry represents a potential market of approximately 10,000 TPD of oxygen and 4,500 TPD of nitrogen. However, this market does have fairly stringent product purity requirements – 90 to 98% oxygen purity and 99.999% nitrogen purity. A fuel saving is the main driver for oxygen-enriched combustion in the glass industry, consequently the cost of oxygen must be low enough to provide significant economic incentive. Because the opportunity for co-products in the glass market is so large, this market offers an enormous potential for energy savings – provided the demanding product purity requirements can be met with oxygen-selective PSA technology. At this time, the greatest barriers to commercial use of oxygen selective adsorbents for bulk air separation are lack of materials with suitable properties, and concerns about their use in oxygen rich environments.

### Trace Oxygen Removal

As outlined to DOE, an initial commercialization opportunity for oxygen selective adsorbents is post-purification of crude nitrogen from commercial membrane or carbon molecular sieve systems. We view this application as a beneficial step in the commercialization of oxygen selective adsorbents for bulk separations since it can provide market acceptance for this new adsorbent technology. Preliminary process evaluations using the best available data for equilibrium, kinetics, cost, and lifetime indicated the technical feasibility of nitrogen purification by **IA-3**. Accurate mass transfer data have now been determined and were used in combination with equilibrium data to update the process model. Process economics for purification of crude nitrogen using **IA-3** indicate that this new technology can successfully compete with alternative supply options in the US for a relatively narrow production rate window. It appears likely that the commercialization incentives will be higher in other geographies and this is being verified by Praxair regional organizations. Commercial opportunities will continue to be pursued by Praxair after the conclusion of the DOE program. Commercialization of this new class of adsorbents for purification applications may ultimately reduce the cost incentive that is required to adopt a similar technology for bulk air separation.