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Energy in the
Southwest

Kurt S. J. Anderson
Editor

The New Mexico Academy of Science

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The *New Mexico Journal of Science* is the annual publication of the New Mexico Academy of Science. Each issue of the journal, which has been published since 1960, contains research papers and review articles deemed of interest to the scientists, educators, and citizens of New Mexico. Some volumes have addressed topics of social or economic interest to the state while others have emphasized scientific areas in which New Mexico is particularly active. Authors have usually been drawn from the universities, colleges, and research institutions of New Mexico.

This year's *Journal*, subtitled "Energy in the Southwest", follows in that tradition. Energy matters are of particular interest in a state which is a major energy producer and in which fully 15% of the state government's General Fund Revenues are derived from leases and severance taxes on oil and natural gas production. Revenues derived from these activities on State Trust Lands support the schools and hospitals of New Mexico. While these resources are large, they are limited, and the revenues generated from their exploitation strongly subject to fluctuations in market prices. However, New Mexico's wind energy capabilities are growing and the state's research institutions are vigorously engaged in the development of new solar, geothermal, and biofuel technologies. New Mexico university groups are also leading efforts in those areas of waste management and water resources related to the production and distribution of energy.

In a break with tradition, this 2008 volume of the *Journal* is being published in an electronic-only format. Production costs are the main reason for this change; the Editor hopes that we will be able to also provide a paper edition in future years.

The research papers in this volume have been reviewed before being accepted for publication. The Editor wishes to thank those anonymous reviewers for the efforts toward maintaining the quality of this publication.

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New Mexico Academy of Science

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New Mexico Journal of Science

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Energy in the Southwest

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Energy Production in New Mexico; Past, Present and Prospects

Kurt S. J. Anderson¹

Abstract

New Mexico is a major United States producer of coal, oil and natural gas. Its borders contain major reserves of these fuel materials and the largest deposits of uranium in the United States. These reserves, with the exception of the last, are likely to be exhausted within a few decades at current rates of extraction. Environmental considerations, mainly those affecting water resources, are the principal current constraints upon production. The near future of New Mexico as a net energy producer probably lies in the production of solar- and wind generated electricity. The state also has major geothermal resources, which remain to be exploited.

ENERGY PRODUCTION

New Mexico is a leading producer of oil and natural gas, most of which is currently exported to other states for refining, conversion, and/or consumption. The major oil and gas deposits are to be found in the Permian Basin in the southeastern part of the state and in the San Juan Basin of the northwest. The San Juan Basin, which extends into Colorado, contains the largest proved natural gas reserves in the United States. The Permian Basin, which extends into Texas, contains some of the most productive fields in the country. New Mexico also extracts a significant amount of coal, most of which (about 60%) is used for the production of electricity within the state, the remainder being put to similar use in neighboring Arizona. The majority of New Mexico's coal mines are to be found in the San Juan Basin. (About a third of the state's natural gas production is coalbed methane.) The Energy Information Administration (EIA 2008) publishes "State Energy Profiles" which contain energy production and consumption details for each state. These profiles can be found on their website at <http://tonto.eia.doe.gov/state/>. The information in the following table indicates New Mexico's current status as an energy producer and consumer and is drawn from this source (EIA 2008). The numbers correspond to circumstances in late 2008.

New Mexico: Production, consumption, and proven reserves as a percentage of US totals

| Resource | Production | Consumption | Reserves |
|--------------|------------|-------------|----------------------------|
| Oil | 3.5% | 0.7% | 3.4% |
| Natural Gas | 8.3% | 1.0% | 7.3% (dry), 9.2% (liquids) |
| Coal | 2.1% | 1.5% | 2.5% |
| Uranium | - | - | 35% |
| Total Energy | 4.0% | 0.7% | - |

New Mexico's crude oil refineries represent about 0.7% of the national refining capacity, but even this is sufficient to process only about three-quarters of the state's oil production.

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It should be noted that dividing the estimate of proved crude oil reserves by the current crude oil production rate gives a resource lifetime of just over 12 years. Similar calculations for natural gas and coal give about 11 years and 20 years, respectively. (The numbers are all drawn from the table entitled “Reserves & Supply” in EIA 2008.) New Mexico’s energy future would not seem to lie in the extraction of coal, oil, or natural gas.

Finally, New Mexico and Wyoming contain most of the country’s domestic uranium reserves. Historically, these two states would rank fourth and fifth among the countries of the world in terms of past production. However, significant uranium mining is not now occurring in New Mexico (Kamat 2006, 2007). The future of that industry is strongly tied to that of nuclear power production in the United States - which currently generates about 19% of its electricity in this way.

ELECTRIC GENERATION

New Mexico generates almost one percent of the nation’s electric power but, mainly because of its relatively small population and a relative dearth of energy-intensive industries, exports much of that. Fully 78% is provided by coal-fired plants, 18% by natural gas-fired facilities, about 3% from various renewable resources, primarily wind generation. Hydroelectric and oil-fired electricity production is negligible, representing about 0.5% of the total. New Mexico currently has no commercial nuclear power facilities.

WATER ISSUES

“Whiskey is for drinking; water is for fighting over.” - attributed to Mark Twain

While New Mexico is rich in many natural resources, water is not one of them. The use and allocation of water resources is the subject of ongoing legal battles within New Mexico and with neighboring states. (The effect upon whiskey consumption has yet to be determined.) The relative scarcity of water and the potential for damage to such resources as are present will severely constrain any expansion of coal, oil, and gas production in New Mexico. History suggests that similar concerns would arise in connection with any resurgence in uranium mining.

The extraction of oil and gas requires considerable amounts of water during well-drilling stages and water is often subsequently injected for enhanced recovery. That injected water is laced with a witches’ brew of chemicals including scale and corrosion inhibitors, emulsion breakers, and biocides. Much of this returns from wells as “produced water” which has the potential to contaminate surface waters if not confined or otherwise treated; subsurface waters can be damaged as well. Furthermore, a large amount of water is used in the oil refining process. New Mexico refineries presently use from 10.6 to 39.1 gallons of water per refined barrel (42 US gallons) of crude oil and generate 6.5 to 25.4 gallons of wastewater per barrel (Timm 1985)

Significant amounts of water are also used to transport coal. Water and pulverized coal are mixed (in roughly equal proportions) to produce a liquid slurry, which can be easily transported by pipeline and even burned as a fuel in place of oil. Water contamination through acid mine drainage is an additional concern. “Coal slurry” usually refers to the mixture of solid and liquid wastes which is produced in large quantities during coal mining and coal preparation operations.

Slurry impoundments can be large and pose potential threats to water supplies. Similarly, seepage from old uranium mines and tailings piles threatens both the surface waters and the underlying aquifers at several locations in New Mexico (*e.g.*, ATSDR 2008)

Agriculture currently makes major demands upon water resources in New Mexico, and chemical contamination by agricultural runoff is of some concern to downstream users. Water issues associated with these agricultural uses are likely to be raised again in the context of future production of biofuels. Among developing technologies only wind- and solar energy generation seem likely to have relatively little impact on New Mexico's rather limited water resources.

RENEWABLE ENERGY TECHNOLOGIES

Most renewable energy technologies are aimed toward the production of electricity, either directly (wind, solar, ...) or through intermediary fuels (methane, ethanol, ...). New Mexico's Net Summer electric power production capacity in 2006 was about 7.1 gigawatts, about 0.7% of US capacity, of which 582 megawatts, or about 8% of the total, was based upon renewable sources. (EIA 2008). Then, as now, wind generation provided about 85% of that renewable capacity, hydropower about 14%, and biomass the remaining one percent. Geothermal and solar production was negligible. Future energy production in New Mexico will increasingly be based upon renewables, with probable emphases upon the expansion of wind generation capabilities, the development of solar power technologies, and perhaps the exploitation of the state's considerable geothermal resources. The rôle of bioenergy production in New Mexico is less clear; to the extent it based upon traditional agricultural methods it will be constrained by land use and water issues.

There are some legislated incentives for the development of renewable energy facilities in New Mexico. The New Mexico Public Regulatory Commission Portfolio Standards for Renewable Energy require that by 2011 public utilities in New Mexico must acquire or generate at least ten percent of their electricity from a renewable resources such as solar, wind, or hydroelectric installations. As of September 2008 that figure stood at about 3.7% (EIA 2008).

Wind Generation

“The answer, my friend, is blowin' in the wind.” - Dylan 1962

New Mexico currently ranks seventh among the states in terms of installed wind capacity according to the American Wind Energy Association and twelfth in terms of its wind energy potential (AWEA 2008). The estimated potential of 49.7 gigawatts average power output is a hundred times the current wind generation capacity or about 150 times the current annual electricity generation rate in New Mexico (AWEA 2008, EIA 2008). While there are only four wind power plants now operating in New Mexico the potential for further development is great; the most promising regions for “wind farms” are on the eastern plains of the state. Moreover, the current cost of wind generated power in New Mexico, is now less than \$0.04 per kilowatt-hour, lower than that of fossil fuel sources. Finally, it is important to note again that wind power development has little negative impact upon water resources. It would seem that wind power has a promising future in New Mexico.

Solar Power

The state of New Mexico offers a number of incentives, through tax credits, subsidies, and protective legislation, for the installation of solar photovoltaic and heating systems in residences and businesses. As of 2008 there are no utility-scale solar power facilities operating in New Mexico. However, a (potentially) 300-megawatt photovoltaic facility is under construction near Deming, New Mexico and scheduled for completion in 2011 (FP 2008). If fully completed as envisioned, this would be thirty times the size of any existing photovoltaic system in the world. For comparison, current wind generation capacity is about 500 megawatts. Moreover, a request for proposals has been issued by a consortium of utilities for the construction of an 211 to 375 gigawatt-hour per year solar thermal facility in New Mexico. New Mexico and Arizona contain the premier sites within the United States for the placement of solar facilities, a consequence of their relatively low geographical latitudes and abundant year-round sunshine. The solar power production potential in New Mexico exceeds that of any other state. (WIPP 2008)

Bioenergy

The burning of wood for residential heating is still the principal use of biomass for energy production in New Mexico. A small amount of heating and electricity generation comes from the burning of methane produced by municipal waste treatment plants. (Methane is the principal constituent of natural gas remaining after its processing for commercial use.) About a half-dozen cities (including Albuquerque and Las Cruces) generate methane from wastewater sludge to power their sewage treatment facilities. Similarly, some sawmills burn waste wood to provide heat for their drying kilns. Bioenergy currently produced in the state is generally consumed at the place of origin. However, New Mexico does have one sorghum-based ethanol production facility in Portales that produces about 15 million gallons of ethanol. (Southwest Farm Press News 2005). In any case, current bioenergy generation is negligibly small in comparison to wind generation and even hydroelectric production in New Mexico. (ECMD 2009)

Most recent bioenergy developments in New Mexico involve the production of methane as a byproduct of municipal sewage or agricultural waste treatment efforts. A sizable dairy industry produces a considerable quantity of manure and on-site bioreactors are being developed to process this waste to produce methane.

Agricultural production of biofuels (*e.g.*, corn ethanol) usually requires both suitable lands and ample water supplies. Both are at a premium in New Mexico, and these forms of biofuel production will have to compete with food crops for these relatively scarce resources. As a renewable energy source the production of biofuels offers less promise in New Mexico than the direct production of electricity from wind or solar power.

Geothermal Power

The most significant present use of geothermal resources in New Mexico is for the (hot water) heating of greenhouses. A single geothermal power production facility was constructed in the Animas Valley in 1995 and was capable of producing about 750 kilowatts of electric power before it was shut down two years later (Fleishman 2006). A new geothermal plant was constructed nearby in 2008, and is expected to be producing 10 megawatts of electric power in 2009, and 25 megawatts in a planned second phase (Steffen 2008). For comparison, current wind

generation capacity in New Mexico is about 500 megawatts, and solar power facilities of comparable capacity are under construction (*cf. supra*). However, geothermal resources can operate continuously and are not subject to the diurnal and seasonal fluctuations of solar insolation nor to the vagaries of wind and cloudy weather.

Estimates of the potential for electric generation from geothermal systems are highly uncertain and depend upon completeness of the geothermal surveys, the temperatures of the sources, the local permeability of the Earth's crust, and the technologies available to exploit the resource. The U.S. Geological Survey provides an updated assessment of geothermal resources in the United States (Williams, et al., 2008), which indicates that New Mexico ranks about seventh in terms of its geothermal potential for electric generation. In terms of identified sources that capacity is only about 0.17 gigawatts (1.9% of the US total) but an estimate of likely undiscovered sources raises that capacity to 1.48 gigawatts (5% of the US total). Drilling into high temperature regions rather than relying on the natural permeability of the surface layers to water can enhance heat recovery. To the extent these technologies might be employed New Mexico's geothermal potential increases considerably, to about 56 gigawatts or about 11% of the US total capacity under these assumptions (Williams, et al. 2008). This is similar to the wind generation potential for the state (*cf. supra*). For comparison, New Mexico's current electric generation capacity is about 7.1 gigawatts (EIA 2008) and is largely coal-based.

SUMMARY

New Mexico is a major United States producer of coal, oil and natural gas and contains major reserves of these fuel materials; but these reserves will soon be exhausted at present rates of extraction. Environmental considerations affecting the state's water resources are the principal current constraints upon further exploitation of these nonrenewable resources. New Mexico also has major uranium reserves, which are not currently being used; the future of this resource is more promising than oil, gas, or coal, but dependent upon the extent to which the United States turns more to nuclear power for electric generation.

The future of New Mexico as a net energy producer probably lies in the production of solar- and wind generated electricity. Geothermal production of electricity offers considerable promise, particularly if enhanced recovery technologies can be implemented. At present, the technology for wind generation seems to be the most advanced and is the only method producing significant electric power in New Mexico. With current technology it is also the cheapest to implement and operate on a cost per energy unit basis.

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NUCLEAR ENERGY AND WASTE DISPOSAL IN THE AGE OF FUEL RECYCLING

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Sondra Sage¹
Judith Wright²

ABSTRACT

The magnitude of humanity's energy needs requires that we embrace a multitude of various energy sources and applications. For a variety of reasons, nuclear energy must be a major portion of the distribution, at least one-third. The often-cited strategic hurdle to this approach is nuclear waste disposal. Present strategies concerning disposal of nuclear waste need to be changed if the world is to achieve both a sustainable energy distribution by 2040 and solve the largest environmental issue of the 21st century – global warming. It is hoped that ambitious proposals to replace fossil fuel power generation by alternatives will drop the percentage of fossil fuel use substantially, but the absolute amount of fossil fuel produced electricity will be kept at or below its present 10 trillion kW-hrs/year. Unfortunately, the rapid growth in consumption to over 30 trillion kW-hrs/year by 2040, means that 20 trillion kW-hrs/yr of non-fossil fuel generated power has to come from other sources. If half of that comes from alternative non-nuclear, non-hydroelectric sources (an increase of 3000%), then nuclear still needs to increase by a factor of four worldwide to compensate. Many of the reasons nuclear energy did not expand after 1970 in North America (proliferation, capital costs, operational risks, waste disposal, and public fear) are no longer the intractable problems once thought. The WIPP site in New Mexico, an example of a solution to the nuclear waste disposal issue, and also to public fear, is an operating deep geologic nuclear waste repository in the massive bedded salt of the Salado Formation. WIPP has been operating for eight years, and as of this writing, has disposed of over 55,000 m³ of transuranic waste (>100 nCi/g but <23 Curie/liter) including some high activity waste. The Salado Formation is an ideal host for any type of nuclear waste, especially waste from recycled spent fuel. From the standpoint of addressing operational and environmental risk, as well as public fear, WIPP has had extensive human health and environmental monitoring. The Carlsbad Environmental Monitoring and Research Center at New Mexico State University, located in Carlsbad, NM, has been the independent monitoring facility for the area around WIPP from 1993 to the present, i.e., from six years before disposal operations began to nine years of waste disposal operations (www.cemcr.org). Based on the radiological analyses of monitoring samples completed to date for area residents and site workers, and for selected aerosols, soils, sediments, drinking water and surface waters, there is no evidence of increases in radiological contaminants in the region of WIPP that could be attributed to releases from WIPP.

THE ROLE OF NUCLEAR IN ACHIEVING A SUSTAINABLE ENERGY DISTRIBUTION BY 2040.

As we approach global peak oil availability in the next ten years, we must be able to diversify into the many other energy sources available in order to achieve a sustainable energy production that will allow the North American economy to grow without intermittent shortages, security vulnerabilities, extreme costs or environmental degradation (Wright and Conca, 2007). Energy distribution depends strongly upon the locality (Table 1) with the United States having more coal and nuclear than the world at large. Using best-estimate population growth and global energy consumption projections (United Nations 2004), world population will exceed 9 billion by 2050 and energy consumption will top 40 trillion kW-hrs/year (Figure 1, and Deutch & Moniz 2006). With determined conservation and efficiency programs, this might be reduced to 30 trillion kW-hrs/year, although present trends indicate this to be unlikely (Energy Information Administration, 2007, Stix 2006). Ambitious replacement proposals of fossil fuel (coal, oil and gas) power generation by alternative energy sources hope to drop the percentage of fossil fuel use by half from its present 67% to 33% (Figure 2). Unfortunately, because of the rapid growth in consumption, 33% of 30 trillion kW-hrs/year is 9.8 trillion kW-hrs/year, which is the same absolute amount of fossil fuel used today (Figure 1). This means that CO₂ emissions will not drop appreciably, and CO₂ capture, sequestration, or other technologies will have to solve the emission problem.

Therefore, if we are successful in cutting fossil fuel use to 33%, the remaining 20 trillion kW-hrs/yr of generated power must come from other sources than non-fossil fuel (Figure 1). If half of this, or 10 trillion kW-hrs/yr, comes from alternative non-nuclear sources (an increase of 3000% and beyond any anticipated goal), then nuclear still needs to increase by a factor of four to compensate. If not, fossil fuel use will double and CO₂

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TABLE 1. Energy Distribution by Country or Region.

| | |
|-----------------------|----------------------|
| <i>World</i> | <i>Canada</i> |
| 8% oil | 33% oil |
| 39% coal | 9% coal |
| 20% gas | 25% gas |
| 17% nuclear | 7% nuclear |
| 15% hydroelectric | 25% hydroelectric |
| <i>European Union</i> | <i>United States</i> |
| 30% coal | 50% coal |
| 18% gas | 19% gas |
| 32% nuclear | 19% nuclear |
| 11% hydroelectric | 6% hydroelectric |
| 6% oil | 6% other |
| 3% other | |
| <i>New Mexico</i> | <i>California</i> |
| 88% coal | 21% coal |
| 10% gas | 41% gas |
| 2% other | 13% nuclear |
| | 17% hydroelectric |
| | 8% other |

World Power Consumption
(trillion kiloWatt-hours per year)

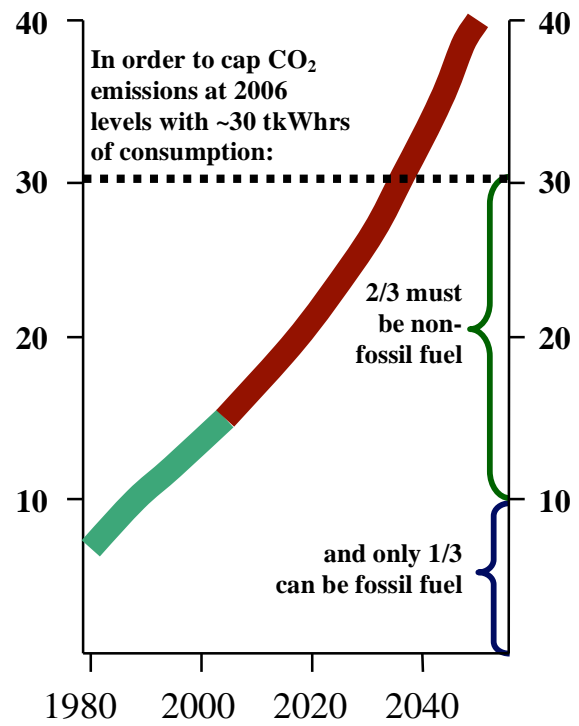


Fig. 1. World energy consumption from 1980 projected to 2050. It is imperative that this levels at about 30 trillion kW-hrs/year in order to be able to cap CO₂ emissions at present levels. After Deutch & Moniz (2006).

concentrations in the atmosphere will exceed even 600 ppm. France is an example of how this strategy can be successful. Between 1980 and 1987, when France implemented its changeover to nuclear energy, generating 80% of its power from nuclear, its CO₂ emissions dropped from 134 million tons/year to 96 million tons/year, at the same time electricity consumption increased 46%. This is the only instance in the world where a major energy-producing country has met the goals of the Kyoto protocol, indeed many times over as this rolled France's emissions back to 1960s levels. Therefore, in order to address global warming and long-term energy sustainability, nuclear energy production must increase significantly, and all countries including the United States need to begin ambitious and sustained construction of new design nuclear power plants to reduce the number of new fossil fuel power plants anticipated over the next generation. Fully 1500 nuclear plants are needed by 2040.

ADDRESSING NUCLEAR ISSUES

Nuclear energy slowed substantially in the 1970's for several reasons, one of which was that the United States abdicated its leadership role. The main concern was fear of proliferation, an issue that has become less U.S.-centric with the increase in enrichment capabilities worldwide, with new fuel and reactor designs, and with the possible eventual adoption by the world community of some type of nuclear energy partnership in which nuclear fuel is provided to non-nuclear-capable countries by nuclear countries thereby removing the necessity of non-nuclear countries from developing enrichment capabilities of their own that can be used to produce weapons-grade material.

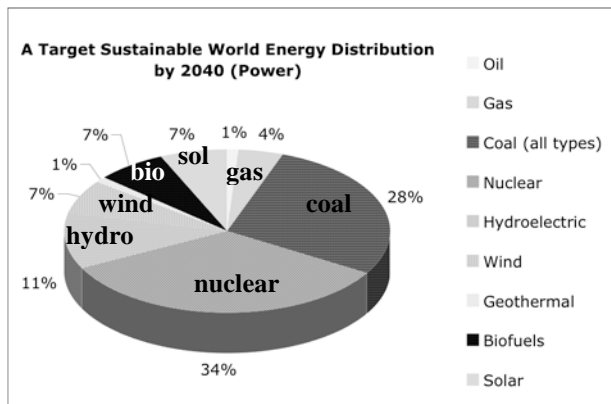
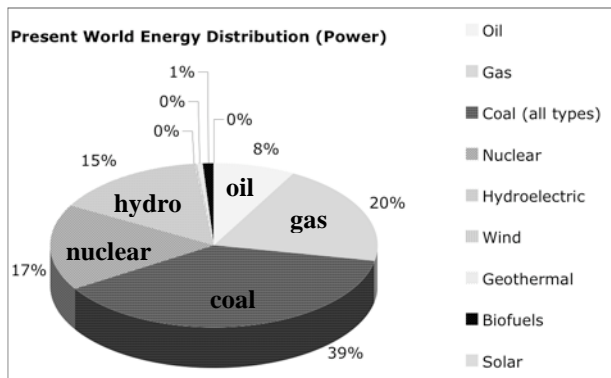


Fig. 2. Present world energy distribution (above) and a 2040 target distribution (1/3 fossil fuel, 1/3 renewables and 1/3 nuclear).

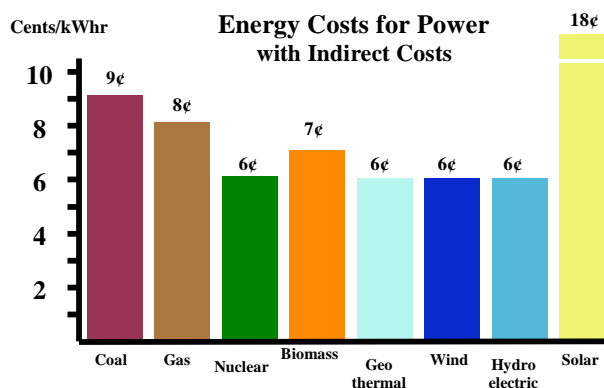
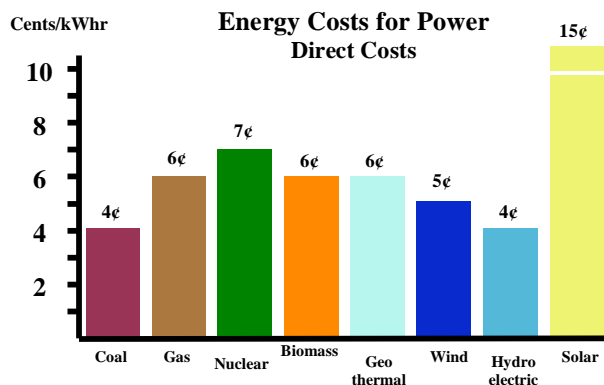


Fig. 3. Energy Costs/kWhr in the U.S. determined as direct costs (above) and indirect costs (below) which factors in environmental and footprint costs.

Since the fuel costs are much lower than the O&M costs of nuclear power (23% fuel vs. 77% O&M), unlike coal (78% fuel vs. 22% O&M) or gas (91% fuel vs. 9% O&M), this makes economic sense (OECD 2005, NEI 2006). The user country does not need to enrich or dispose, and proliferation is greatly controlled if not removed. The key to success is the ability to recycle spent fuel in the nuclear countries to a sufficient degree to replace fuel as needed and to reduce disposal volumes. If proliferation is no longer the main problem, then the four remaining problems cited against nuclear energy are capital costs, operational risks, public fear, and waste.

Capital costs can be addressed by standardizing reactor designs. Having four or five generic power plant designs would reduce costs and streamline the regulatory process, as occurred in France during the 1990s. Also, new life-cycle costs for all energy sources must factor in indirect costs such as carbon tax, environmental costs and footprint costs as are captured by the European Union's ExternE monetization methodologies (Bickel & Friedrich 2005), and disposal costs. Life-cycle energy costs are shown in Figure 3, with coal the least expensive at 4 cents/kW-hr, and nuclear at 7 cents/kW-hr (Bickel & Friedrich 2005, Deutch & Moniz 2006, Jochem 2006, Kammen 2006, see also websites listed for: Atomic Energy of Canada Limited, U.S. Department of Energy, Energy Information Administration, Association for the Study of Peak Oil and Gas, National Renewable Energy Laboratory, National Energy Institute, American Association of Petroleum Geologists, International Atomic Energy Agency, U.S. Geological Survey, Canadian Center for Energy).

When monetization methodologies are factored into these costs, particularly footprint and carbon taxes, life-cycle energy costs become 9 cents/kW-hr for coal, 8 cents/kW-hr for gas, and only 6 cents/kW-hr for nuclear, becoming as inexpensive as wind. Once built, nuclear energy is the least costly, most efficient energy source there is, with costs just above a penny/kWhr. Nuclear energy has a capacity factor (CF) of 92%, the highest of any energy source (CF ~ 30% for wind, CF ~ 55% for coal) which means the plant is operating almost all the time at nearly full capacity and with constant and dependable output. Finally, nuclear is the only energy source not subsidized by

federal and state governments, but is burdened with nuclear taxes and extremely high finance rates resulting from unwarranted public unease.

The issues of operational risks and public unease can only be addressed by public education, continued monitoring of the existing sites and reactors, and adoption of standardized designs. Even including Chernobyl, the textbook case of a poor design coupled with an incredible degree of human error, the nuclear industry has the safest record of any industry. Standardization would remove any future Chernobyl-type events. In contrast, Americans unwittingly accept over 200,000 deaths each year from iatrogenic means (properly performed medical procedures and prescription drug use), 160,000 from tobacco, 110,000 from alcohol, 60,000 from automobile accidents and 20,000 from the use of coal, yet live in constant fear from the zero deaths per year in the nuclear industry. Even for non-lethal injuries like falling off a ladder or cutting a finger with an exacto-knife, the nuclear industry is the safest. More injuries occur in an office trading stocks than in a nuclear power plant. This extreme inequity and ignorance must be driven home more forcefully.

The remaining issues of nuclear waste disposal and uranium mining can be addressed by recycling spent fuel, and rethinking disposal of that waste stream in a permanent, non-retrievable deep geologic repository.

NUCLEAR WASTE

The critical aspect about nuclear waste unknown to the public and public officials is that there is not much of it. All the spent fuel generated in the United States in the last 60 years can fit on a single soccer field (assuming a PWR assembly dimension of 21.5 cm x 21.5 cm, approximately 100,000 used assemblies, and a regulation soccer field of 100 x 60 yards). Compared to that, the over 100 million tons of solid waste and 2 billion tons of CO₂ generated from coal-fired power plants each year is staggering. Even worse is the greater than 500 million tons of solid chemical and sanitary waste generated each year, and the 2 quadrillion gallons of water requiring waste treatment each year. These are large waste volumes. All the nuclear waste generated in the United States in a thousand years can fit into one repository. It is interesting to note that, while not high enough to be a health concern, living near a coal-fired power plant provides a greater radiation dose than living near a nuclear power plant. This is because coal-fired power plants generate about 3,000 tons of U, Th and their daughter products each year, a small amount compared to the 800 million tons of coal fuel, but still more than the 600 tons of spent fuel generated each year from nuclear. Recycling would reduce this amount of nuclear waste even more.

Contrary to public opinion, nuclear waste is easy to handle, because there is so little of it and radiation is so easy to measure. Unlike chemicals and biologicals, we have been measuring radiation for 80 years, and it has been difficult to get a serious dose. This is why, since commercial nuclear power began in the United States, no one has died or been seriously injured by nuclear waste or by working at a nuclear power plant, the best safety record of any industry or any job.

CHARACTERISTICS OF A GEOLOGIC REPOSITORY FOR RECYCLED NUCLEAR WASTE

Looking beyond the current Yucca Mountain repository program, characteristics of a suitable geological repository for the disposal of nuclear waste from an expanded fleet of U.S. nuclear reactors might include the following favorable characteristics (McEwen 1995, EPRI 2006)

- i. a simple hydrogeology,
- ii. a simple geologic history,
- iii. a tectonically interpretable area,
- iv. isolation robustly assured for all types of wastes (no vitrification or reforming necessary),
- v. minimal reliance on engineered barriers to avoid long time extrapolation of models for certain types of performance,
- vi. performance that is independent of the canister, i.e., canister and container requirements are only for transportation, handling and the first several hundred years of peak temperature after emplacement in a repository, and
- vii. a geographic region that has an existing and sufficient sociopolitical and economic infrastructure that can carry out operations without proximity to a potentially rapidly growing metropolis (unlikely to ever have human habitation anywhere near the site).

These characteristics are similar to an optimal repository for spent nuclear fuel except that there is no requirement of retrievability, since the recycle waste has already been reprocessed to remove useful components. Especially

important is the removal of the need to vitrify higher-activity waste prior to disposal in a repository that meets these criteria.

Two rock types that fit these characteristics are argillaceous rocks (claystones and shales) and bedded salts. Many studies have focused on argillaceous sites, particularly in Canada and Europe with some strong technical arguments (Nuclear Energy Agency 2001); similarly for salt deposits (McEwen 1995, National Academy of Sciences 1970). Although salt deposits exist throughout the world (Zharkov 1984), many are not sufficiently massive, have too many clastic interbeds, are tectonically affected, or are near population centers. Salt domes and interbedded salts are less optimal than massive bedded formations from a hydrologic standpoint, particularly within the United States where diapiric movement can exceed 1 mm/yr (McEwen 1995) and spline fractures can act as hydraulic conduits. Still, there are many viable salt deposits globally that meet these criteria (Zharkov 1984, Waughugh & Urquhart 1983, Karalby 1983).

MASSIVE BEDDED SALT OF THE SALADO FORMATION

The Salado Formation in the Permian Basin of southeast New Mexico is one such formation that satisfies all of the above characteristics. The Salado Formation is a massive bedded salt deposit that has a simple hydrogeology with no dual-porosity or multi-component properties. The Salado has had a simple geologic history and is in a tectonically quiet area. The Salado is a simple geologic unit exhibiting self-healing rock mechanical properties, such that the host rock cannot maintain open and connected fractures or pores, resulting in an overall hydraulic conductivities $\leq 10^{-14}$ m/s (Beauheim & Roberts 2002) and diffusion coefficients $\leq 10^{-15}$ m²/s (Beauheim & Roberts 2002, Conca *et al.* 1993). The unit provides performance that is independent of waste type, engineered barriers, and water content. The unit provides an environment that does not require long-term, or even short-term, survival of the canister. Container requirements are only for transportation and handling pre-placement. Geographically, there are many sites underlain by the Salado Formation that are remote from human habitation yet have sufficient socioeconomic infrastructure to support disposal operations.



Fig. 4. The Waste Isolation Pilot Plant (WIPP), the only operating deep geologic nuclear waste repository, is excavated 700 meters below the surface in the massive salt of the Salado Formation, and has operating successfully since 1999.



Fig. 5. Over 10,000 nuclear waste drums and standard waste boxes filling 1 of 56 rooms to be filled at WIPP over a 20-year period. Almost 25 rooms have been filled as of June 2008. Note the higher activity remote handled waste plunged into boreholes in the wall to the right and plugged.

If these properties and conditions sound familiar, it is because the Salado Formation is already host to an operating deep geologic nuclear waste repository, called the Waste Isolation Pilot Plant, or WIPP, shown in Figure 4. WIPP, near Carlsbad, NM has been operating for over nine years and, as of this writing, has disposed of over 55,000 m³ of waste in over 100,000 containers, equivalent to about 280,000 fifty-five gallon drums (Figure 5, see also <http://www.wipp.energy.gov>).

But recently, WIPP has begun accepting waste containing radionuclides that emit more penetrating gamma radiation, referred to as Remote Handled (RH) waste. RH waste has surface exposures greater than 200 mrem/hr, so must be shielded and remotely handled. It still must have transuranic activity concentrations greater than 100

nanocuries per gram of waste, but the upper limit is 23 Curie/liter. These higher activities mostly result from gamma emissions from the decay of isotopes such as ^{137}Cs and $^{90}\text{Sr}/^{90}\text{Y}$. This upper limit is similar to processed high-level waste such as high level waste sludge or its treated form as vitrified glass. The RH waste is shielded, shipped in a 72B casket (Figure 6), and inserted remotely into a horizontal borehole in the disposal room wall (at right in Figure 5). These boreholes are single-drum-width in diameter and three drum-lengths deep with a shield plug, and are emplaced on 8-ft centers along the wall, similar geometrically to many international high-level waste disposal strategies. Another unique feature of the Salado is the ease, safety and low-cost of mining operations versus hard rock.

An important issue relating to disposal of reprocessed waste, or any high-thermal waste, in the Salado Formation is the presence of fluid inclusions in the salt. The water content in the salt is extremely low (between 0.5 and 1.5% by volume) and exists primarily as fluid inclusions of brine and brine along grain boundaries. Fluid inclusions have been studied extensively with respect to high activity waste disposal because inclusions can migrate under a significant thermal gradient, e.g., $1.5^\circ\text{C}/\text{cm}$, by dissolution of salt on the up-gradient side and re-precipitation on the down-gradient side (Roedder 1984). This process encourages brine to migrate towards the waste. In most international high-level waste programs, this has been viewed as a problem because the canisters and any engineered barriers are required to survive intact anywhere from 10,000 to 100,000 years and interactions with brine, however small the volumes, could be detrimental to canister performance. However, in the Salado Formation, the canister does not need to survive after emplacement, there is no need for engineered barriers, and a halo of increased water content within or around the disturbed rock zone is of no consequence from a repository performance standpoint.

In addition, after fluid inclusions have migrated and the salt has recrystallized behind them, the hydraulic conductivity is still $< 10^{-12}$ m/s and the diffusion coefficient is even lower because of the lowered water content (Conca *et al.* 1993). In fact, at WIPP, the performance assessment assumes a repository with various amounts of water inundation probabilistically distributed, from dry to completely flooded, with completely breached and corroded containers. Therefore, fluid inclusion migration is not an issue for nuclear waste disposal in the Salado Formation or any other salt deposit with similar characteristics (McEwen 1995; Beauheim and Roberts 2002).

VII. ENVIRONMENTAL MONITORING

From the standpoint of addressing operational and environmental risk, as well as public fear, WIPP has had extensive human health and environmental monitoring from six years before operations began to over nine years of waste disposal operations (Carlsbad Environmental Monitoring and Research Center 2007). The Carlsbad Environmental Monitoring and Research Center is in the Institute for Energy and the Environment, in the College of Engineering at New Mexico State University. Located in Carlsbad, NM, CEMRC has been the independent monitoring facility for the area around WIPP from 1993 to the present (www.cemcr.org). Based on the radiological analyses of monitoring samples completed to date for area residents and site workers, and for selected aerosols, soils, sediments, drinking water and surface waters, there is no evidence of increases in radiological contaminants in the region of WIPP that could be attributed to releases from WIPP. Levels of radiological and non-radiological analytes measured since operations began in 1999 have been within the range of baseline levels measured previously, and are within the ranges measured by other entities at the State and local levels since well before disposal phase operations began in 1999. Constituents and properties measured by the monitoring program in these media include, but are not limited to, gross alpha/beta, ^7Be , ^{212}Bi , ^{213}Bi , ^{214}Bi , ^{144}Ce , ^{249}Cf , ^{60}Co , ^{134}Cs , ^{137}Cs , ^{152}Eu , ^{154}Eu , ^{40}K , ^{233}Pa , $^{234\text{m}}\text{Pa}$, ^{212}Pb , ^{214}Pb , ^{106}Rh , ^{125}Sb , ^{208}Tl , ^{228}Ac , ^{234}U , ^{235}U , ^{238}U , ^{230}Th , ^{232}Th , ^{228}Th , ^{241}Am , ^{238}Pu , $^{239,240}\text{Pu}$, various VOCs, and many inorganic constituents normally analyzed in waters, particularly RCRA constituents. The *in vivo* bioassay (whole body counting) program at CEMRC participates in the Department of Energy's *In Vivo* Laboratory Accreditation Program (DOELAP) via WIPP, and is currently accredited to perform the following direct bioassays - transuranium elements via L x-ray in lungs, ^{241}Am , ^{234}Th , ^{235}U , fission and activation products in lungs including ^{54}Mn , ^{58}Co , ^{60}Co and ^{144}Ce , and fission and activation products in total body including ^{134}Cs and ^{137}Cs (and ^{57}Co , ^{88}Y and ^{133}Ba).

As an example of monitoring results, the gross alpha and beta activities for airborne particulate matter (aerosols) collected from WIPP exhaust air is shown in Figure 7 for the last eight years, expressed as *activity concentrations*, calculated as the activity per unit volume of air sampled (mBq m^{-3}). Data points are distinguished by color, with red being pre-disposal, blue being operational, and black being Station A backup results. The minimum detectable activity concentrations for gross alpha were ≈ 0.1 mBq m^{-3} , while for gross beta is ≈ 0.2 mBq m^{-3} . Aerosols have been the major focus of the monitoring effort because, in the event that radioactive or chemical contaminants are

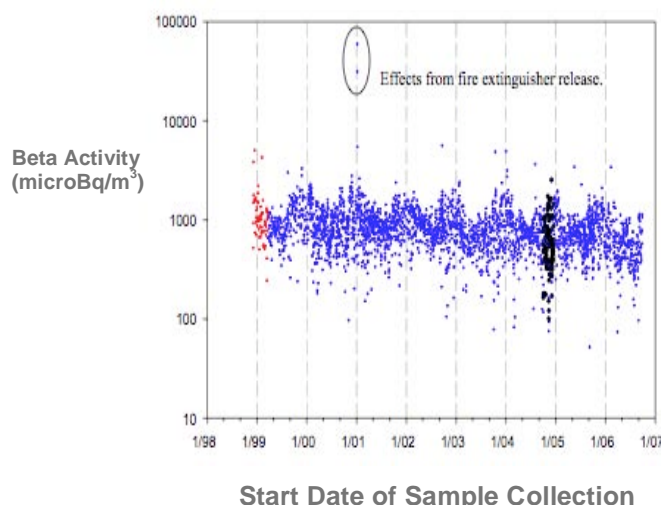
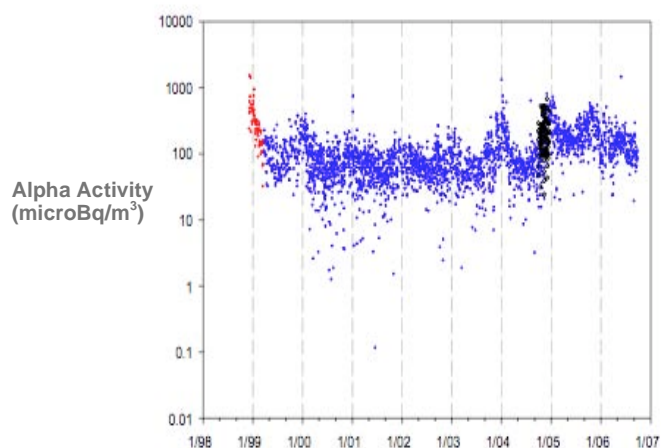


Fig. 6. Remote Handled nuclear waste (>100 nanoCi/gram of waste but <23 Ci/liter), some of it from reprocessing, being transported to the WIPP site in New Mexico in a 72B cask.

Fig. 7. Timeseries plots of gross alpha and gross beta activity concentrations of aerosols on filters sampling air exiting the WIPP underground (Station A FAS). Red points denote pre-disposal samples, blue points are for operational samples and black points are for samples collected with the back-up sampler.

released from WIPP, these materials could be rapidly dispersed through the atmosphere and spread throughout the environment. CEMRC monitors two types of aerosols in the area of WIPP. Station A, an above-ground fixed air sampling platform, provides a way to monitor for releases of radionuclides and other substances in the exhaust air from the WIPP (Figure 7). Station A is located where radioactive or hazardous materials would most likely first be detected in the event of a release. CEMRC commenced sampling of the WIPP exhaust air at Station A on December 12 1998. The samples are collected on 47 mm diameter membrane filters with the use of a shrouded probe, commonly referred to as a fixed air sampler or FAS. The airflow through the FAS is approximately 170 liters per minute. The FAS sample filters are normally changed daily. All the analyses of the FAS filters are performed according to methods detailed in CEMRC document-controlled, standard operating procedures. After the samples are returned to the laboratory, the individual filters are first weighed to determine mass loadings, and after allowing for the decay of short-lived radon daughters, they are counted for gross alpha/beta activities for 1200 minutes using a low-background gas proportional counter (a Canberra LB4100 and, starting in 2006, a Protean MPC9604).

The essence of the strategic design for the monitoring program, including the studies at Station A, has been to compare pre- vs. post-disposal data. The first radioactive waste shipments were received at the WIPP on March 26, 1999, and this is considered the cut-off date separating the pre-disposal phase from the post-disposal or operational phase. The WIPP first received mixed waste on September 9, 2000, and therefore data for samples collected prior to that date compose a pre-mixed waste baseline for the elemental data while those collected afterwards are considered operational. The gross alpha and beta activities (Figure 7) in the samples collected prior to the receipt of the first waste shipment represent the pre-disposal background, and the bulk of the activity in those samples was due to naturally occurring radioactive materials, specifically radon daughters. As shown in Figure 7, the pre-operational

gross alpha activity concentrations were high compared with the annual mean values for the next five years. Gross alpha and beta activities exhibit clear seasonal variability with peaks occurring in winter. An especially pronounced annual cycle in alpha activity concentrations, with high values in December and January and low values mid-year is seen in 2004 to 2005. After 2005, alpha activities appear to have gone back up to pre-operational levels, while beta remains slightly lower than pre-operational levels.

After gross alpha and beta measurements, elemental and gamma-ray analyses are conducted on weekly composites of the FAS filters. Individual FAS filters are digested using a mixture of strong acids in a microwave digestion unit, and weekly composites were prepared from the digestates of the individual filters. The weekly composites are then analyzed for a suite of trace elements with the use of a Perkin-Elmer Elan inductively coupled plasma-mass spectrometry (ICP-MS). The ICP-MS methods can provide data for up to ~35 elements, but in practice the concentrations of some elements, including As, Be, Cd, Er, Eu, Sc, Se, Sm, Tl and V are often below detectable or quantifiable levels, and a second set of elements (notably Ag, Li and Sn) has variable concentrations in blank filters which makes their quantification difficult. Analyses of gamma emitters are performed on the same weekly composites as used for the elemental studies; gamma analyses are done using a low-background, high-purity Ge well detector and a count time of 24 hours.

Finally, quarterly, or more recently, monthly composites are prepared from the weekly composites, and these are used for the determination of actinide activities. Only one half of the composite sample is normally used for the determination of the actinide activities. The remaining aliquot is archived. The composite sample is evaporated to dryness, and the residue is digested in perchloric acid to destroy the black residue, which consists mostly of diesel exhaust particulates. This process ensures that fluorine is completely removed and all traces of organic filter residue have been oxidized. The actinides are then separated as a group by co-precipitation on $\text{Fe}(\text{OH})_3$. After dissolution, Pu, U, and Am are separated by anion exchange and extraction chromatography, and the sample planchettes are finally prepared for alpha spectrometry using rare-earth micro-coprecipitation.

Figure 7 also shows the sensitivity of the monitoring program that was demonstrated in January 2001 when CEMRC found two samples with elevated gross beta activity concentrations in the Station A sample filters. Follow-up investigations eventually traced the source of the beta emitters to the discharge of a fire extinguisher underground, but the incident was more notable because it demonstrated for the first time the ability of the monitoring system to detect a non-routine event. A second, more significant incident occurred when scientists from CEMRC reported that they had detected a small quantity of Pu in a composite aerosol sample from the second calendar quarter of 2003. This discovery was later corroborated by other site monitoring programs through the analyses of samples that were independently collected and analyzed. The activity was extremely low and well-within historic ambient air background, but indicated the ability of the monitoring program to detect radionuclides of interest at any level above the MDC.

In addition to environmental monitoring, WIPP has addressed public concerns by developing a network of acceptable nuclear waste transportation routes throughout the United States, including many diversion routes around population centers. WIPP's perfect safety record has gone a long way towards increased public acceptance and confidence. Finally, the issue of remoteness from population centers is handled very well by the Salado Formation near WIPP, where the nearest towns are over 30 miles away (Carlsbad, Hobbs, Eunice, Otis and Loving, NM) and the nearest cities are well over 100 miles away (Roswell, NM and Midland, Lubbock and El Paso TX).

VIII. CONCLUSIONS

Massive salt deposits, such as the Salado Formation near Carlsbad, New Mexico, offers a ready solution to the disposal of nuclear waste from reprocessing spent fuel, a major impediment to solving our power generation and environmental needs in the next fifty years. This unit is already host to permanently disposed nuclear waste at the WIPP site. The extensive scientific investigations of this unit, a perfect safety record over the nine years of operation, and the recent disposal of higher-activity remote handled nuclear waste, demonstrate the capability of massive salt deposits, and of this type of operational environment, to handle nuclear waste of any type. Especially important is the removal of the need to vitrify higher-activity waste prior to disposal. Various salt and clay formations throughout the world can also serve as suitable nuclear waste repositories, having similar physical and isolation properties. From the standpoint of addressing operational and environmental risk, as well as public fear, any nuclear repository must have extensive monitoring of human health and the environmental, beginning from before operations, on the public, waste disposal workers, aerosols, water and soils.

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Pressure Swing Adsorption Process for Carbon Dioxide and Moisture Removal from Air

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Shain J. Doong²

Pressure swing adsorption pre-purification unit (PSA PPU) is a recent technology for air purification in certain types of air separation plants. Typically activated alumina based adsorbents are used for removing both moisture and carbon dioxide from ambient air before the cryogenic separation of air. It was observed that carbon dioxide concentration plateau forms in the activated alumina bed under certain operation conditions. The carbon dioxide concentration plateau significantly reduces the process efficiency and interferes with process control and optimization. This research aims at understanding the mechanism of carbon dioxide concentration plateau formation through adsorption process simulation. Adsorption process simulation was performed to investigate the process performance of pressure swing adsorption for air purification. Accurate adsorption isotherm data of both carbon dioxide and water on activated alumina were correlated with a modified D-A equation and applied to the gas mixture adsorption equilibrium prediction. The key of the simulation is to successfully predict the carbon dioxide concentration profiles including the carbon dioxide concentration plateau inside the adsorbent bed. Preliminary simulation results indicate that the simulation package developed for bulk separation can also be used for trace removal if appropriate adsorption equilibrium and kinetic data are employed. The predicted concentration of carbon dioxide in the purified air from a simple PSA process is less than 3 ppb, which agrees well with the experimental results obtained in a pilot plant study. This represents a significant improvement over the reported simulation results on PSA air purification.

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1. Introduction

Oxygen and nitrogen, two of the top ten chemicals produced worldwide, are separated from air by either cryogenic distillation, or pressure swing adsorption depending upon the volume of production and product purity [12]. In addition to nitrogen, oxygen and argon, ambient air contains many trace impurities. These impurities include moisture, carbon dioxide, oxides of nitrogen, light hydrocarbons and others. For cryogenic air separation plants, these impurities may be classified into four groups: plugging compounds, flammable compounds, reactive compounds and corrosive compounds [5]. It is critical to remove these trace impurities from ambient air prior to fractionation of the air into its major components (oxygen and nitrogen) to ensure a safe and economical operation of the cryogenic air separation plants [3, 4, 5]. Traditionally the trace impurities in ambient air were removed by the reverse-heat-exchange in old cryogenic air separation plants. These days, the air pre-purification in the modern cryogenic separation plants is carried out primarily by adsorption [3, 4, 5].

The removal of water and carbon dioxide from air by selective adsorption of these before air separation into oxygen and nitrogen by cryogenic distillation is well known [1, 3, 4, 5]. When the adsorbent beds become laden with adsorbed water and carbon dioxide, the adsorbent is regenerated. Such adsorption of contaminants and regeneration of the adsorbent may be carried out by various known techniques which can be characterized as employing either temperature swing adsorption (TSA) or pressure swing adsorption (PSA). PSA is more recent technology than TSA [1, 3, 4, 5]. However it is being accepted as the method of choice for many air pre-purification plants. The primary differences between these two processes are [5]:

- (1). The adsorbents used for purification are different in the two processes. Equilibrium isotherms for the adsorbents used in TSA PPU are more non-linear than for the adsorbents used in PSA PPU. Typically zeolite 13X is used in the temperature swing adsorption pre-purification units (TSA PPU) and activated alumina-based adsorbents are used in the pressure swing adsorption pre-purification units (PSA PPU) [1, 3, 4, 5].
- (2). TSA processes require thermal energy to regenerate the adsorbent. PSA requires compression energy. Therefore, TSA may be a preferred option if a cheap source of energy is available. However, if this is not the case, the total energy cost for a PSA PPU is lower than for a TSA PPU.

(3). The cycle time for PSA processes is much shorter than that for TSAs (several minutes vs. several hours). This is because the effective working capacity for the PSA PPU is lower than that of TSA PPU. This results in larger bed volumes for PSA PPU than for TSA PPU for the same cycle time. Therefore, to keep the vessel sizes reasonable, the cycle times for PSA PPU are reduced. This results in choosing a TSA PPU for very large air separation plants, and PSA PPU for small to medium plants.

(4). PSA requires much larger quantities of purge gas than TSA (40% vs. 10% of feed air). Therefore, a TSA process is preferred if available purge gas quantity is in short supply. This may be the case when the plant produces multiple products at high recoveries.

(5). Although the average trace impurity concentrations in the purified air from TSA and PSA processes may be same, the peak impurity concentrations in the purified air are quite different in these two processes. There is no impurities breakthrough into the purified air in the TSA process until the last period of adsorption step. However, there is a constant level of impurities in the purified air in the PSA process.

The major differences between the TSA PPU and the PSA PPU call for different approaches for designing and operating these two processes. The focus of this paper is to address one of the very critical issues in PSA PPU design and operation - understanding and predicting the impurity concentration profile inside the adsorbent beds in a PSA PPU cycle. Adsorption process simulation was used to elucidate the formation mechanism of carbon dioxide concentration plateau inside the alumina-based adsorbent beds in a PSA PPU process.

2. Pressure Swing Adsorption Cycle for Pre-Purification of Air

The PSA PPU cycle for pre-purification of air studied in this work, as shown in Figure 1, was developed at BOC in the early 1990s [3]. It is a typical two-bed Skarstrom's cycle [10]. The main steps in the BOC PSA PPU cycle include:

1. Product re-pressurization: after the purge step, the regenerated bed is re-pressurized with purified air stream prior to going onto the next adsorption step. The re-pressurization step typically lasts 1-5 minutes. The use of product for re-pressurization can preserve the bed concentration profile and therefore increase the product purity.
2. Feed/Adsorption: trace impurities including water, carbon dioxide and others are removed from the air by adsorption on a selective adsorbent, generating a purified air stream which is fed

to the cryogenic air separation plant. Activated alumina-based adsorbents are typically used in PSA PPU because of their relatively high working capacity for both water and carbon dioxide removal under PSA mode [1, 3]. The adsorption step typically lasts about 5–30 min, and is operated at close to ambient temperature. The feed pressure varies from 3 to 10 atm.

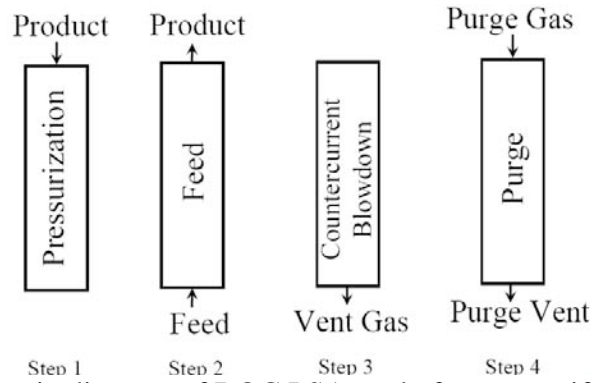


Figure 1. Schematic diagram of BOC PSA cycle for pre-purification of air [1].

3. Countercurrent blowdown: when the carbon dioxide concentration in the purified air streams reaches a predetermined level (ppb), the adsorption step is terminated, and the pressurized gases in the adsorber are vented to atmosphere for a short period of time (about 1–2 min). The pressure and temperature in the vessel after venting are close to ambient conditions.
4. Countercurrent purge: although some adsorbed gases are desorbed during the venting step, the adsorbent needs further regeneration to recover its working capacity. Normally a low pressure carbon dioxide free dry gas stream generated as waste from the cryogenic distillation column is used to purge the PPU vessel to regenerate the adsorbent at close to ambient temperature. The purge step time is usually shorter than adsorption step time.

It was observed in lab studies and plant operations that a concentration plateau of carbon dioxide forms inside the activated alumina adsorbent beds in the PSA PPU under certain operation conditions [1]. As shown in Figure 2, the carbon dioxide in air is effectively removed from the feed concentration (350 ppm) to less than 0.1 ppm by the first 30% of the adsorbent layer, then a carbon dioxide concentration plateau covers next 50% of the bed, and the final 20% of the adsorbent layer removes carbon dioxide to ppb level. The existence of the carbon dioxide concentration plateau reduces the PSA PPU process efficiency for carbon dioxide removal, and increases the difficulty for process design and operation. The mechanism for carbon dioxide concentration plateau formation is not clear, and it is difficult to predict and eliminate the

concentration plateau in PSA PPU. The focus of this work is to describe the carbon dioxide and water concentration profiles with the adsorption process simulator developed at BOC [6, 9], and to elucidate the formation mechanism of the carbon dioxide concentration plateau.

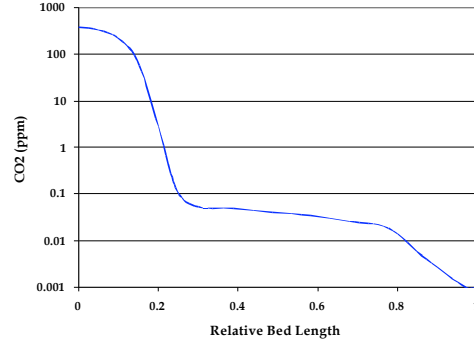


Figure 2. Concentration profile of carbon dioxide inside activated alumina adsorbent bed during adsorption step in a PSA PPU process [1].

3. Adsorption Process Simulation of PSA Cycles for Pre-Purification of Air

3.1 PSA Model

To simplify the PSA PPU simulation only three components, 350 ppm CO₂, 3000 ppm H₂O and N₂, were considered to be present in the ambient air. The isotherm data of CO₂, H₂O and N₂ on activated alumina adsorbent H-156, a composite adsorbent of zeolite 4A and activated alumina from Alcoa [1, 3], were obtained from different sources and used for prediction of the performance of a PSA air pre-purification process using a computer simulation model. The mass balance equation (Eq.1) for component *i* in the adsorbent bed is given by the axially dispersed plug flow equation [7-9, 11], and a linear driving force model (Eq.2) is used to account for the mass transfer resistance. The corresponding energy balance equations, which were solved in the simulation for temperature profiles, can be found elsewhere [7-9, 11].

$$-D_L \frac{\partial^2 C_i}{\partial z^2} + u \frac{\partial C_i}{\partial z} + \frac{\partial C_i}{\partial t} + \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial \bar{q}_i}{\partial t} = 0 \quad (1)$$

$$\frac{\partial \bar{q}_i}{\partial t} = k_i (q_i^* - q_i) \quad (2)$$

3.2 Adsorption Equilibrium Model

A modified Dubinin-Astakhov (D-A) adsorption equation (Eq. 3) was applied to correlated the single component adsorption isotherm data [2, 7]. It was also used to predict the

adsorption equilibrium for gas mixtures in this work. The CO₂ isotherm on H-156 was measured at BOC; it is quite different from that used in Rege's work [7] as shown in Figure 3(A). The H₂O and N₂ isotherm data are similar to those used by Rege *et al.* [7].

$$n = k_1 \exp\left(\frac{k_2}{T}\right) \exp\left[-\left(k_3 T \ln \frac{P_s}{P}\right)^m\right] \quad (3)$$

3.3 Numeric Method

Eq.1 along with energy balance equations constitute a set of nonlinear partial differential equations, coupled with the rate equation, Eq. 2. A finite difference method was employed to convert them into ordinary differential equations. Standard time integrators such as Runge Kutta or Gear method were then used to solve them. Boundary and initial conditions can be written based on the steps of the PSA process. It takes more than 800 cycles to reach the cyclic steady state depending on initial conditions and process parameters. The computation time for one cycle in a Pentium-IV PC is between 2 to 20 minutes depending on grid size. The adsorption process simulator developed at BOC [6, 9] was modified by using the modified D-A equation for the PSA PPU simulation in this work.

4. Results and Discussion

The linear driving force coefficient k_i was obtained by fitting the experimental data of CO₂ concentration profile with the simulator. The CO₂ concentration profile, as plotted in Figure 3(B), was obtained on H-156 adsorbent at 5 bara, 40 C and purge to feed ratio (P/F) of 1.7. Purge to feed ratio is defined as of amount of purge gas used in the purge step divided by the amount of feed gas fed to the adsorbent bed in the adsorption step. As shown in Figure 3(B), the simulation fits the experimental data quite well. It should be pointed out that the calculated CO₂ concentration profile covers the entire range of CO₂ in the feed (350 ppm) and the purified gas (low ppb level). This represents a major improvement over the only publication on PSA PPU simulation in the open literature [7]. The PSA PPU simulation results reported by Rege *et al.* [7] showed more than 10 ppm of CO₂ in the purified gas at similar operating conditions. The key to successful prediction of ppb level CO₂ in the product is the application of accurate CO₂ isotherm in our simulation.

The same linear driving force coefficient k_i obtained from the regression discussed above was used in the simulation runs discussed in this work. 500 cycles of PSA PPU were carried out

to study the transient behavior of CO₂ and H₂O concentration profiles. The calculated CO₂ and H₂O concentration profiles at end of 100, 200, 300, 400 and 500 cycles are plotted in Figure 4(A). It was observed the H₂O concentration profile stabilized after about 100 cycles, while the CO₂ concentration profile changed very slowly with cycle number. This agrees well with observation from PSA PPU experiments. The calculated H₂O concentration profiles also match well with Rege's data because the H₂O isotherm data used in this work are similar to those used in the reported work [7].

It was also observed in a simulation run that CO₂ concentration plateau can be eliminated if the P/F ratio is increased. This was clearly shown in Figure 4(B). The PSA PPU cycle was started with an initial CO₂ concentration plateau, the plateau disappeared after about 300 cycles after increasing the P/F from 1.4 to 1.7. This suggests that CO₂ plateau formation is a transient behavior determined by the operating conditions.

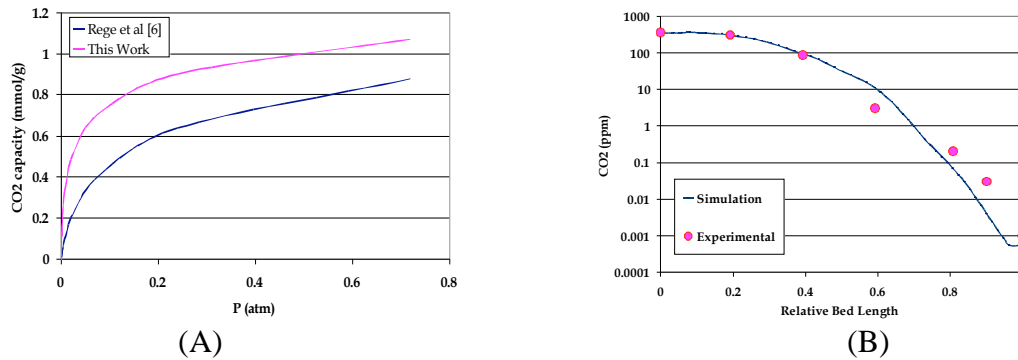


Figure 3. (A). Adsorption isotherms of CO₂ on alumina adsorbents used in this work and those by Rege *et al.* [7]; (B). Expt. CO₂ concentration profile (H-156, 5 bara, 40 C, P/F=1.7) vs. simulation results

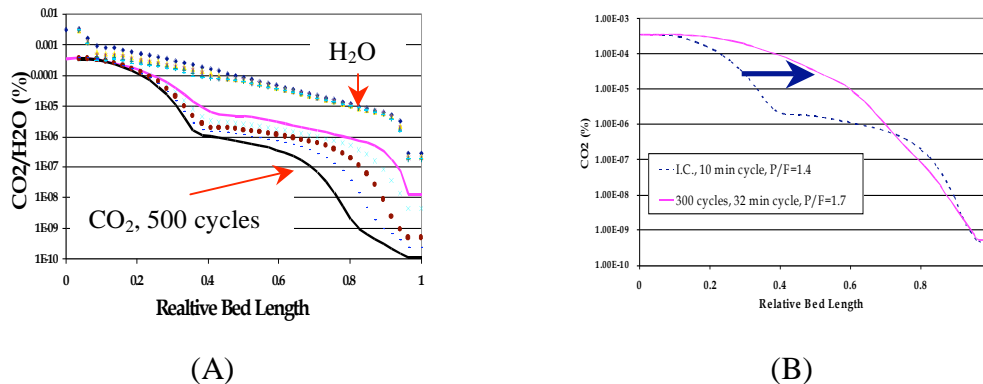


Figure 4. (A). Simulation results of H₂O and CO₂ concentration profiles variations in 500 cycles (H-156 adsorbent, 32 min. per cycle, 3.5 bara, 25 C, P/F=1.4); (B). Simulation results showing CO₂ concentration plateau eliminated by increasing the P/F ratio (H-156 adsorbent, 32 min. cycle time, 3.5 bara, 25 C)

5. Conclusion

The PSA process simulator developed at BOC was able to describe the concentration profiles to low ppb levels of CO₂ and H₂O in the PSA pre-purification of air. The predicted CO₂ concentration profiles match well with the pilot plant results. The key to the successful simulation of the air purification process is to apply accurate adsorption equilibrium data for both CO₂ and H₂O. It was observed in both experiments and simulation that CO₂ profiles change very slowly in the cyclic runs; and a CO₂ concentration plateau forms at certain unfavorable operating conditions. The simulation results also showed the feasibility of eliminating the CO₂ concentration plateau by increasing the purge to feed ratio, which strongly suggests the transient behavior of the CO₂ concentration plateau.

Acknowledgements

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Deep Desulphurization of Hydrocarbon Fuels for Fuel Cell Applications

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Sulfur removal from hydrocarbon fuels is an important effort to reduce air pollution and a necessary step to protect the reforming catalysts and electrocatalysts in fuel cell power supply systems. The reduction of sulfur in hydrocarbon fuels has been largely accomplished by hydrodesulphurization. Although the new regulations proposed much lower allowable sulfurs in hydrocarbon fuels, the sulfur concentration in the fuels is still too high for direct fuel cell applications. The residual sulfurs in the fuels including thiophene, benzothiophene, dibenzothiophenes and their alkylated derivatives can be removed by selective adsorption. This paper reports the development of sol-gel derived mesoporous γ -alumina-based ruthenium adsorbents and their applications in removing organic sulfurs from hydrocarbon fuels based on sulfur-selective adsorption mechanism. Sol-gel wet-impregnation and sol-solution mixing methods were applied to prepare the mesoporous γ -alumina-based adsorbents. Adsorption breakthrough of thiophene from a RuO₄/ γ -alumina adsorbent bed was obtained and analyzed with the Klinkenberg breakthrough model.

1 Introduction

The removal of sulfur compounds from liquid fuels is becoming a very important task worldwide in recent years because of more stringent environmental regulations and the emerging needs for producing high purity hydrogen as a fuel for fuel cells, which require less than 0.004 $\mu\text{mol/mol}$ or 4 ppbv of total sulfur in hydrogen for mobile and stationary applications [9]. The U.S. Environmental Protection Agency (US EPA) Tier II regulations require reductions of sulfur in diesel from 500 to 15 parts per million by weight (ppmw) by June 2006 and reductions of sulfur in gasoline from 350 to 30 ppmw by January 2005 [1]. Similarly stringent new regulations are being implemented in other countries.

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A research work on sulfur effects on H₂-O₂ fuel cell performance, as plotted in Figure 1, has clearly shown that even 1 ppmv of H₂S in H₂ could permanently poison the fuel cell anode catalyst[4]. This result could well justify the very stringent requirement of only 4 ppbv of total sulfur in the fuel cell-grade hydrogen proposed by International Organization of Standardization (ISO/PDTS 14687-2) [9]. This creates a very challenging fuel purification problem for the scientific and technology community.

Figure 1(B) outlines three sulfur removal options for fuel cell applications:

(1). For certain small fuel cell power generators hydrocarbon fuels are the choice of fuels due to their high energy density, availability and storage convenience. Typically, the hydrocarbon fuels are converted into hydrogen through a small on-board reformer, and the hydrogen is subsequently fed into anode of a proton exchange membrane fuel cell to produce electricity. The sulfur in the fuels must be removed to less than 1 ppmw to protect the reforming catalyst and the fuel cell anode catalyst. Conventionally the organic sulfur compounds are removed in a catalytic reactor with hydrogen at high temperature and high pressure in refineries. The future transportation fuels produced under the new regulations will contain 15-30 ppmw of sulfurs in the form of thiophene, benzothiophene, dibenzothiophene, and their alkylated derivatives [10, 11]. The residual sulfur compounds will most likely be removed by a selective adsorption process. The key of this adsorption process is to identify a suitable adsorbent with high selectivity for the sulfur molecules.

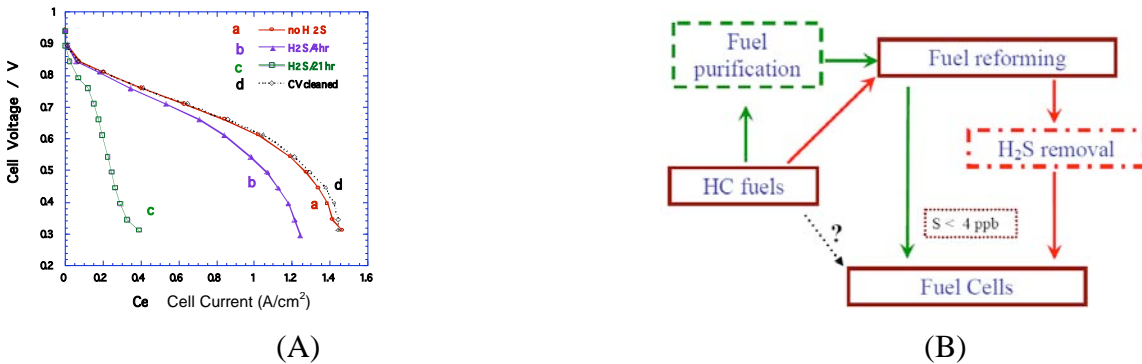


Figure 1. (A). Sulfur effect on H₂-O₂ fuel cell performance (1 ppmv of H₂S injection to anode) [5]; (B). Sulfur removal options for fuel cell applications.

(2). With the advance of reforming technology, especially the development of sulfur-tolerant reforming catalysts, it is possible to feed the low sulfur (15-30 ppmw sulfur) transportation fuels

directly into a reformer to produce hydrogen for the fuel cells. The sulfur compounds in the hydrocarbon fuels will convert into H_2S that needs to be removed to below 4 ppbv before H_2 enters the fuel cells.

(3). The ideal solution is to feed the low sulfur hydrocarbon fuels directly into the fuel cell system, which requires novel fuel cell electrolyte materials and sulfur-tolerant electrocatalysts that can directly oxidize the fuels. So far this can be done only with sulfur-free light hydrocarbons in solid oxide fuel cells [12].

Selective adsorption of sulfur compounds from liquid hydrocarbons is an interesting and challenging task [6, 8, 10, 11]. As pointed out by Yang [10, 11] conventional adsorbents are ineffective for desulphurization of hydrocarbon fuels due to the strong competitive adsorption between the hydrocarbons, especially benzene and its derivatives, and the sulfur molecules. Non-conventional adsorbents reported in the literature have success in removing sulfur compounds from hydrocarbons and can be classified into three categories: (1) Yang's π -complexation adsorbents [10, 11]; Song's desulphurization catalyst-based adsorbents [8]; and ruthenium-based sulfur-selective materials [6]. The sulfur-selective adsorbents look promising because they could potentially extract the sulfur only from the sulfur-containing compounds. However, the sulfur-selective materials reported by Angelici's group are used in a liquid-liquid extraction process, which is not efficient due to poor mass transfer. This research aims at improving the mass transfer of the sulfur-selective materials by dispersing the active components onto a mesoporous alumina support.

2 Sol-Gel Derived Mesoporous Alumina-Based Adsorbents

A sol-gel technique developed in our previous research [2,3] was applied to synthesize pure activated alumina and activated alumina supported ruthenium oxide adsorbents. Both sol-solution and sol-gel/wet-impregnation methods were used for preparation of new activated alumina-based adsorbents [2, 3].

The sol-gel derived mesoporous adsorbents prepared in this work were characterized with nitrogen adsorption (Micromeritics, ASAP 2020) for their pore textural properties. The typical nitrogen adsorption and desorption isotherms on the sol-gel derived alumina adsorbents at 77K are shown in Figure 2(A), the corresponding pore size distribution calculated from the desorption isotherm is plotted in Figure 2(B). As summarized in Table 1, three adsorbents with about 10

wt.% of RuO₄ on γ -Al₂O₃ were synthesized with wet-impregnation and sol-solution mixing methods. Their pore textural data were determined from the BET measurements discussed above. Powder X-ray diffraction (Siemens, CuK α 1) was used to determine the adsorbent phase structure, and X-ray fluorescence spectrometer (Kevex Omicron 952-7) was used for determining the adsorbent composition. The XRF spectra identifying alumina and ruthenium peaks are shown in Figure 3(A). The concentrations of RuO₄ in the adsorbents are about 10 wt.%.

Table 1. Pore Textural Properties of Three RuO₄/ γ -Al₂O₃ Adsorbents

| Sample No | BET (m ² /g) | Pore Volume (cm ³ /g) | Pore diameter (Å) | Preparation Method |
|-----------|-------------------------|----------------------------------|-------------------|--------------------|
| 1 | 244 | 0.30 | 42 | Sol-solution |
| 2 | 223 | 0.25 | 41 | Sol-solution |
| 3 | 155 | 0.27 | 56 | Wet-impregnation |

3 Adsorption of Thiophene on RuO₄/ γ -Al₂O₃ Adsorbent

3.1 Adsorption Breakthrough of Thiophene

Adsorption breakthrough experiments were carried out in a vertical glass column (ID: 1 cm) packed with 20 grams (15.7 cm³) of RuO₄/ γ -Al₂O₃ adsorbent (No. 3 in Table 1). A solution containing 820 ppmw of thiophene in n-hexane was allowed to flow through the column at ambient conditions (25 °C, 1 atm) and at a flow rate of 2 ml/min. Before passing the sulfur contaminated solution through the bed, the adsorbent bed was wetted with a sulfur-free n-hexane solution. Effluent samples were collected at regular intervals of time until complete saturation was reached. The experimental breakthrough curve measured in this work is plotted in Figure 3(B).

A gas chromatography (SRI, 8610C) with a dual flame-ionization-detector (FID) and flame-photometric-detector (FPD) was used to analyze the concentration of thiophenes in n-hexane. It has a low detection limit of 0.2 ppmw for sulfur compounds in hydrocarbons. Similar GC method was used for analysis of organic sulfurs in hydrocarbon fuels by other investigators [8, 10, 11]. It should be pointed out that the resolution of the GC is not sufficient to meet the requirements for fuel cell grade H₂.

3.2 Modeling of Thiophene Adsorption Breakthrough Curve

The partial differential equation governing adsorption breakthrough dynamic behavior can be written as [7]:

$$-D_L \frac{\partial^2 c}{\partial z^2} + \frac{\partial(uc)}{\partial z} + \frac{\partial c}{\partial t} + \frac{(1-\varepsilon_b)}{\varepsilon_b} \frac{\partial \bar{q}}{\partial t} = 0 \quad (1)$$

An analytical solution of a simplified version of the above equation was obtained by Klinkenberg [5] and expressed in the following equations:

$$\frac{c}{c_F} \approx \frac{1}{2} \left[1 + \operatorname{erf} \left(\sqrt{\tau} - \sqrt{\xi} + \frac{1}{8\sqrt{\tau}} + \frac{1}{8\sqrt{\xi}} \right) \right] \quad (2)$$

$$\xi = \frac{kKz}{u} \left(\frac{1-\varepsilon_b}{\varepsilon_b} \right) \quad (3)$$

$$\tau = k \left(t - \frac{z}{u} \right) \quad (4)$$

where ξ is the dimensionless distance coordinate, τ the dimensionless time coordinate, k the overall mass transfer coefficient (m/s), K the Henry constant, u the linear velocity of fluid (m/s), ε_b , the bed porosity, t time coordinate (s), and z the distance coordinate (m).

4 Results and Discussion

The adsorption breakthrough data plotted in Figure 4(B) clearly showed that thiophenes were effectively removed by the RuO₄/ γ -Al₂O₃ adsorbent. Sulfur-free effluent was obtained for about 60 minutes and the mass transfer zone looks very sharp. However, the adsorbent capacity, in terms of sulfur-free fuel produced per unit mass of adsorbent, is 5.5 cm³/g, which is quite lower than the value (34 cm³/g) reported by Yang *et al.* [10, 11]. Part of the reason our adsorbent is not as effective as Yang's is because the monolayer dispersion of the active species (RuO₄) was not achieved, and the BET surface area of the adsorbents prepared in this work (155 m²/g) is less than half of the sol-gel derived alumina adsorbents obtained in our previous studies [2, 3]. Improved adsorbents with higher dispersion of RuO₄ and larger BET surface area should have a higher capacity for sulfur removal from hydrocarbon fuels.

The Klinkenberg solution was used to analyze the thiophene adsorption breakthrough curve measured in the experiments. The Henry constant was obtained by fitting the dynamic equilibrium capacities obtained from several breakthrough runs. Two methods were used to estimate the mass transfer coefficient: convective mass transfer in the film only and the overall mass transfer coefficient including both convective mass transfer and the effective diffusion in the mesopores of adsorbent. As shown in Figure 4(B), the overall mass transfer coefficient method agrees better with the experimental data, which suggests that the diffusion in the mesopores of adsorbent is important. Due to the oversimplifications (negligible axial dispersion) in the Klinkenberg model, the predictions do not match exactly with experimental data. Numerical solution of Eq. 1 is necessary to improve the modeling of the adsorption breakthrough behavior of organic sulfurs on mesoporous alumina adsorbents.

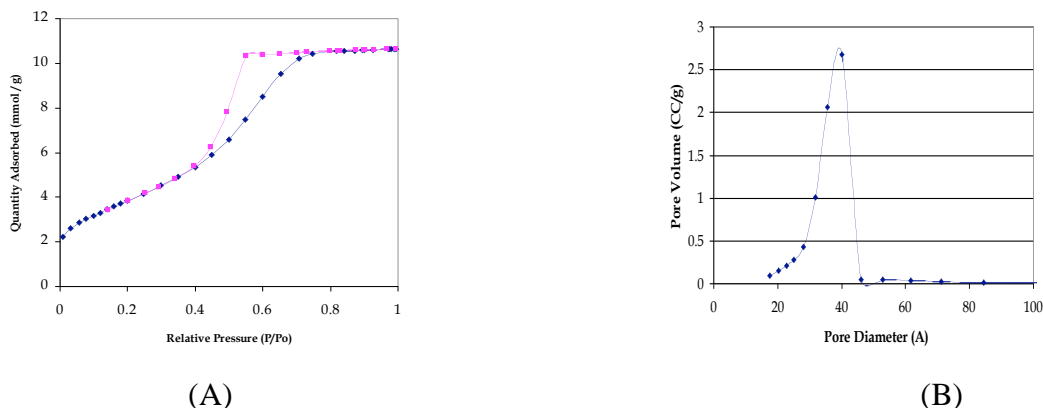


Figure 2. (A). Adsorption and desorption isotherms of N_2 on alumina adsorbent (No. 3) at 77 K; (B). Corresponding pore size distribution of adsorbent No. 3 determined from desorption isotherms in (A).

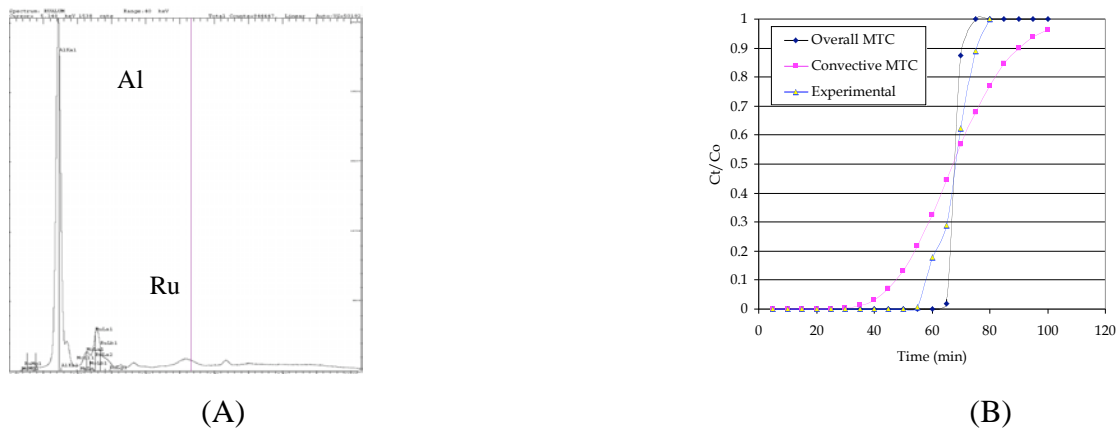


Figure 3. (A). XRF spectra of a $RuO_4/\gamma-Al_2O_3$ adsorbent (No. 3); (B). Adsorption breakthrough curves of thiophene from a $RuO_4/\gamma-Al_2O_3$ adsorbent bed (experimental and simulation results) at 25 °C and 1 atm.

5 Conclusion

Sol-gel technique was applied to synthesize mesoporous alumina supported ruthenium oxide adsorbents for deep desulphurization of hydrocarbon fuels for fuel cell applications. Adsorption breakthrough experiments of thiophene on RuO₄/γ-Al₂O₃ have demonstrated the efficacy of this adsorbent for sulfur removal from hydrocarbon fuels. The adsorbent has an adsorption capacity of 5.5 cm³/g of sulfur-free fuel, and a very sharp mass transfer zone. Analysis of the adsorption breakthrough data with the Klinkenberg model indicates that the diffusion in the adsorbent mesopores is important. It is expected the adsorbent performance can be improved with a better control of synthesis conditions to achieve monolayer dispersion of RuO₄ on alumina with larger BET surface area.

Acknowledgements

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Bioenergy Crop Production in the Four Corners Region

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Abstract

As concerns for increasing costs of petroleum-based energy and global warming continue to mount, research in renewable energy sources has gained global urgency. Since its establishment in 1966, the New Mexico State University Agricultural Science Center at Farmington has been investigating the potential of a variety of crops as sources of bioenergy and environmental enhancement. This research focuses on crop introductions adapted to the region, management strategies for optimum crop production, and the identification of important energy related crop traits.

Starting in 2002, hybrid poplar was initially investigated as a source for wood and fiber products for local mills, but its rapid growth is well suited for bioenergy needs both as a source of combustion fuel and as a feedstock for cellulosic conversion to ethanol. A 2003 study of establishment and early growth of 20 hybrid clones had a five-year mean aboveground biomass of 100 Mg ha⁻¹, and the lead clone, OP-367, produced 208 Mg ha⁻¹. A 2005 collaborative study with GreenWood Resources, Inc. (66 clones) had a mean three-year above ground biomass of nearly 44 Mg ha⁻¹ and the lead clone, once again OP-367, had 120 Mg ha⁻¹ of biomass while three other clones produced over 100 Mg ha⁻¹ of biomass. Collaborating with Washington State University, additional data will be gathered at harvest concerning wood calorific value, cellulose:lignin ratios, and cellulosic fermentation potential. Cellulosic sources of biomass are expected to play a crucial roll in supplying fuel feedstocks as the conversion process becomes more efficient and economical. Additionally, these stands contribute to environmental enhancement by sequestering between 10 and 20 Mg ha⁻¹ of carbon per year.

The center has also conducted research on oilseed crops including sunflower, brown mustard, crambe, canola, and camelina. The recent explosion of interest in biodiesel has spurred breeding programs in both the public and private sector, and as a result the testing program has grown considerably in recent years. In 2006 a test of 16 camelina lines had a mean yield of 1,106 kg ha⁻¹ and the trial leader, Calena, had 1,372 kg ha⁻¹. Oil content averaged 30%. In the same year, a test of 16 canola lines had a mean yield of 1,407 kg ha⁻¹ and trial leader Hyola 401 had 1,800 kg ha⁻¹. Mean oil content was 39%. In 2007, a test of 22 canola lines had a mean yield of 509 kg ha⁻¹, and the trial leader, SW Marksman RR, produced 1,004 kg ha⁻¹. The lower yield was attributed to high temperatures during flowering and an infestation of grasshoppers. Trials continue in 2008 to evaluate adaptation of oilseed crops in the region and evaluate planting dates and other management factors that affect yield.

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The Navajo Agricultural Products Industry (NAPI) was established as a commercial farm to capitalize on water allocated from Navajo Reservoir to the Navajo Nation and to provide jobs as a source of income for resource-poor Navajo residents of the area. The New Mexico State University Agricultural Science Center at Farmington (ASC-Farmington) is located on the Navajo Nation and has long collaborated with NAPI, which is currently irrigating 30,000 ha through center pivot sprinkler systems and raising corn, small grains, alfalfa hay, potatoes, vegetables, fruit, and dry beans.

A crucial role of ASC-Farmington has been to test new crops and crop varieties in our area. The variety trial program, formally named Adaptive Crops Research, has included a diverse range of crops including grains (maize, wheat, barley, and oats), oilseed crops (crambe, canola, camelina, mustard and sunflower), forages (alfalfa and native range grasses), vegetables (onion, potato, tomato, pepper, asparagus, and zucchini), legumes (dry bean, soybean, and chickpea), and fruits (apple, grape, apricot, peach, cherry, and strawberry). Even for crops with a long history in the area, continual testing provides important information on crop adaptability to ever-changing disease and pest pressures, market forces, and crop management techniques. This is the primary entryway for the station to investigate factors related to the production of bioenergy.

Bioenergy production in arid climates can capitalize on substantial solar energy inherent in the region but may be limited by available water. In several river basins, adequate water is available but irrigation strategies have not been developed for short rotation hybrid poplar production. For instance, over 14,000 ha of hybrid poplar plantations under drip irrigation in the arid mid-Columbia River basin are producing approximately 28-35 m³ha⁻¹yr⁻¹ for both biomass feedstock and solid wood products. Likewise, while soybeans dominate the biodiesel markets in the Midwest, other crops are proving to be better suited to arid regions of the western US and Canada.

Hybrid poplar research

When NAPI made the transition from flood and side roll irrigation to center pivots, approximately 4,000 ha of rectangular fields were left idle but with irrigation delivery capabilities intact. Hybrid poplar (*Populus* spp.) presented an opportunity to make use of these rectangular fields with numerous potential environmental and social benefits.

In 2002, a trial of 10 hybrid poplar clones was established at ASC-Farmington to investigate the use of drip irrigation to produce hybrid poplar (O'Neill et al. 2006). The trees were spaced on a 3 by 3-m grid (1,076 trees ha⁻¹) in a 10-year rotation system suitable for growing wood products. Almost immediately, two of these clones showed poor adaptability to our soil conditions (pH ~ 8.2) and despite an attempt at replanting, these clones (50-194 and 184-411) had very poor survival and were dropped from the trial. Otherwise favorable growth rates across the trial and remaining questions led to a trial of 20 clones 2003 to examine leaf chlorosis, growth, and survival on a calcareous soil. This trial was designed as a short-term study, and the trees were spaced much closer at a 1.5 by 1.5-m grid (4,444 trees ha⁻¹) and more closely resemble the densely planted short rotations designed for biomass production. This study had a five-year mean aboveground biomass of 100 Mg ha⁻¹ (20 Mg ha⁻¹ yr⁻¹), and the lead clone, OP-367, produced 208 Mg ha⁻¹ (42 Mg ha⁻¹ yr⁻¹). While survival has remained high in this trial and growth rates vary, some clones have shown that they are not suited for our soil and/or climatic conditions.

These initial trials and the observed favorable growth rates for several tested clones led to collaborative research designed specifically to evaluate hybrid poplar as a source of both combustion fuel and as a feedstock for conversion to cellulose. ASC-Farmington collaborated with GreenWood Resources (GWR) in 2005 to evaluate sixty-six clones under a US Department of Energy biomass production grant. This explicitly energy-related test serves as our main exploration of poplar as a fuel source, but the current results will be related to our results from earlier experiments more directed at wood-product supply. While our primary task in the project is to track growth of the clones, cooperators will be evaluating the trees for specific fuel-related criteria, and these will not be reported here.

Methods and Materials

In spring 2005, 64 hybrid clones were obtained from GreenWood Resources, Inc. of Portland, Oregon to which were added two clones collected locally. Prior to planting, the field was disked, leveled, and sprayed with Roundup. Netafim Ram pressure compensating surface drip line (4.1 l hour⁻¹) with emitters every 1 meter was installed with 1 line per row of trees. Four cuttings per clone per plot were planted April 28 and May 2 and 3, 2005 on 1.6 by 1.6-m spacing. Holes were prepared for cuttings using a length of rebar (1.2-cm diameter) on pre-moistened ground. The 20-cm long cuttings with four to six buds were planted leaving only the top most bud exposed above soil level. Clone entries were replicated in 4 blocks for a total of 1,056 trees. An additional 344 cuttings were planted around the perimeter of the trial for border purposes, resulting in 1,400 trees total.

Although poplar consumptive-use estimates were not available in the Farmington area, monthly water-use rates of first, second, and third season poplars grown at a site having similar climatic characteristics in Oregon were reported by Gochis and Cuenca (2000). These values were used to generate crop coefficients relating to each year of poplar growth as related to growing degree days (GDD). The crop coefficients are then used to modify the Penman-Monteith evapotranspiration value for a given day (ET_{TALL}) and the subsequent values are used to program irrigation. Equation 1 is for first season, Equation 2 is for second season, and Equation 3 is for third and subsequent year hybrid poplar production used at Farmington. Equation 4 calculates the ET value for a given day in a given year of poplar production.

$$KC_1 = 3.93 \times 10^{-1} - 2.58 \times 10^{-5} (GDD) + 5.39 \times 10^{-8} (GDD^2) - 8.98 \times 10^{-12} (GDD^3) \dots\dots\dots (1)$$

$$KC_2 = 3.71 \times 10^{-1} + 1.38 \times 10^{-4} (GDD) + 2.95 \times 10^{-8} (GDD^2) - 8.20 \times 10^{-12} (GDD^3) \dots\dots\dots (2)$$

$$KC_3 = 5.18 \times 10^{-1} + 4.57 \times 10^{-5} (GDD) + 1.19 \times 10^{-7} (GDD^2) - 2.40 \times 10^{-11} (GDD^3) \dots\dots\dots (3)$$

$$ET = KC_{(year)} \times PET \dots\dots\dots (4)$$

Where... KC_(year) = Crop coefficient for a given year
 GDD = Growing degree days
 ET = Evapotranspiration replacement rate (inch)

Irrigation generally begins as soon as water is available (early to mid-April) and proceeds as prescribed by calculated ET, and is terminated in late September or early October.

The soil at the experimental site was originally classified as a Kinnear sandy loam (fine-loamy, mixed, calcareous mesic Typic Camborthid) (Anderson 1970) and later re-classified as a Doak sandy loam (fine-loamy, mixed, mesic Typic Haplargid) (Keetch 1980). Water holding capacity in a 1-m profile is 12.6 cm and pH averages 8.2 resulting in a moderately calcareous

soil that might not be conducive to poplar production. At elevated soil pH, iron availability is reduced resulting in leaf chlorosis (Brady and Weil 1999; Havlin et al. 1999).

Yearly survival, diameter at breast height (DBH), and heights were determined during the dormant season. Wood volume calculations based on Browne's method (1962), as done in previous studies at the center, would be misleading in this study since the variable of interest is total aboveground biomass (TAB) rather than simply bole wood volume. Instead, TAB was calculated after Jenkins et al. (2003). This method for TAB calculation is 'allometric'; that is, it utilizes the relationship between different tree size variables. Regression of the height and DBH of many aspen, cottonwood, and willow stems produces two coefficients specific to the group, and allow us to extrapolate the biomass from a single measured variable per stem: DBH. The number of leaders was counted in the first year of data collection, but in 2006 and subsequent years DBH was measured on multiple stems when they occurred to facilitate a more accurate assessment of biomass.

Statistical analysis was carried out using the ANOVA procedure in the CoStat software package version 6.000 (CoHort 2001). Least significant differences were determined at the 0.05 level.

Results and Discussion

Irrigation plus rainfall for the trial amounted to 1,470 mm in 2005 (additional water was applied over and above calculated ET to aid in establishment), 952 mm in 2006, and 1,040 mm in 2007

Mean first-year survival for the trial was 79 percent as determined in December 2005. Across the four blocks, survival ranged from a high of 88 percent for block 1 (south end of trial) to a low of 70 percent in block 4 (north end of trial). Survival for individual clones averaged over the three remaining blocks ranged from 100 percent to 33 percent. Nine clones had 100 percent survival, and one clone had only 33 percent survival. The remaining 56 clones ranged from 50 percent to 92 percent survival. By the third year in the trial, mean survival (blocks 1-3) had dropped to 78 percent and the number of clones displaying 100 percent survival dropped from nine to four.

The high rate of tree mortality and growth inhibition noted in Block 4 was due to a number of factors. A serious Canada thistle infestation in that area was brought under control by four spot applications of Transline, a clopyralid herbicide. Clay (1991) tested Transline on willows and poplars, and while the willows showed no sign of injury, poplars showed moderate severity of visible damage. However, Clay noted little mortality following injury to poplars. A series of four treatments spread over a year and a half, though, may have had some adverse effect above and beyond that caused by burrowing animals in the root zone. In any case, block 4 is excluded from further evaluations of growth and biomass.

As a means of evaluating chlorosis among the clones, a Minolta SPAD meter was used to assess leaf greenness. A larger number means a greener leaf. Mean SPAD reading for the trial was 38.1, and mean readings for the entries ranged from 20.4 to 51.8. The top 14 entries had significantly higher SPAD readings than the remainder of the trial. SPAD assessment was conducted only in 2005, the first year of the trial.

Based on first year observations, it appeared that several hybrids may exceed OP-367 (entered in this trial as entry 433) in growth and also in tolerance of high pH soils typical of the area. In the first year, entry 10267 ranked first in DBH and height, while clone 433 ranked in the top ten only for basal diameter (only assessed the first year when many trees are less than 1.2

meters tall). In 2006, the first year that total aboveground biomass (TAB) was assessed, entry 433 took the lead producing 17.6 Mg ha⁻¹ during the first two growing seasons. Trial mean TAB in 2006 was 7.8 Mg ha⁻¹. In 2007, entry 433 had amassed a TAB of 119.9 Mg ha⁻¹, and the trial mean had grown to 43.7 Mg ha⁻¹. In terms of growth per year or mean annual increment (MAI) entry 433 was growing at a rate of 39.7 Mg ha⁻¹ yr⁻¹ while the trial on average was growing at a rate of only 14.6 Mg ha⁻¹ yr⁻¹.

Of the 66 *Populus spp.* evaluated (Figure 1) for production in the semi-arid Four Corners region, 42 had *P. deltoides*, 22 had *P. trichocarpa*, and two had *P. nigra* female parentage. There were 24 clones with *P. nigra* male parentage, 23 clones with *P. deltoides*, 11 with *P. maximowiczii*, 6 with *P. trichocarpa* and 1 with *P. balsamifera* male parentage. There were six clones that were the product of *P. deltoides* by *P. deltoides* crosses. Johnson and Johnson (2003) suggest that hybrid poplar breeding programs for the semi-arid regions of eastern Washington and Oregon should include *P. nigra* as one of the parents to increase resistance to poplar-and-willow borer (*Cryptorhynchus lapathi*) and reduce water stress. In this trial, 26 clones meet this requirement.

This trial will continue through 2008 and 2009, and will most likely be harvested in the fall of 2009. At this time, actual tree biomass will be compared to that predicted by the allometric equation and other biofuel-related criteria will be evaluated.

Oilseed crops

Winter canola trials conducted in the early nineties at ASC-Farmington had a mean yield of approximately 1,667 kg ha⁻¹ (Smeal, 1991, 1992, 1994, and 1995). These were line-source irrigation studies in which the prime point of investigation was the effect of decreasing irrigation on yield and the subsequent determination of efficient irrigation management for a canola crop.

With the current interest in biofuels as alternate sources of energy, ASC-Farmington has continued to evaluate oilseed crops for the Four Corners Region. This research is fueled on a regional level by the development of a biodiesel facility in nearby Dove Creek, CO which was contracting with farmers for oilseeds at \$0.24 kg⁻¹ as of 2006 (\$0.40 kg⁻¹ in 2008). In response to this regional need, three collaborative oilseed variety trials were initiated: 1) The Spring Camelina (*Camelina sativa* L. Krantz) Hybrid and Variety Trial, a testing program to help determine which entries will perform best in areas they are tested, was compiled at the University of Nebraska and grown at various locations in the western U.S.; 2) The Spring Canola (*Brassica napus* L.) and Brassica Hybrid and Variety Trial, a program also coordinated through the University of Nebraska; and 3) The Sunflower (*Helianthus annuus* L.) Variety Trial: part of an interstate program in co-operation with Colorado State University (CSU) Agricultural Research Station at Yellow Jacket, CO. While generally coordinated by universities, these trials include varieties developed by public (university) breeding programs as well as private seed and energy companies.

Methods and Materials

All canola and camelina trials were planted in six 25-cm rows and plots were 6 m long. The 2006 canola trial consists of 16 canola lines and 2 brown mustard lines. In 2007, the pool of entries grew to 22, but included no brown mustard. The 2006 camelina trial included 16 lines. In 2006 canola and camelina were planted on April 27, and in 2007 canola was planted on May 1.

Trials were grown under center pivot irrigation in a Doak fine sandy loam. Plots were watered as needed from planting until mid-August both years receiving 549 millimeters of

irrigation and 76 millimeters of precipitation in 2006 and 574 millimeters of irrigation 63 millimeters of precipitation in 2007. In 2006, both canola and camelina trials received dry fertilizer on March 24 (prior to planting and land preparation) at the rate of N 12 kg ha⁻¹, P₂O₅ 58 kg ha⁻¹ and K₂O 68 kg ha⁻¹. During the growing season, 200 kg ha⁻¹ of liquid nitrogen fertilizer was applied through the irrigation water for a seasonal total N 212 kg ha⁻¹ (including the dry fertilizer). For the 2007 canola trial, dry fertilizer was applied on March 20 at the rate of N 12 kg ha⁻¹, P₂O₅ 56 kg ha⁻¹, K₂O 64 kg ha⁻¹, sulfur 3.6 kg ha⁻¹, and zinc 7.3 kg ha⁻¹. During the growing season, 170 kg ha⁻¹ of liquid nitrogen fertilizer was applied through the irrigation water for a seasonal total N 168 kg ha⁻¹ (including the dry fertilizer).

Plots were harvested on September 13 in 2006 and on September 12 in 2007 using a John Deere 3300 combine with a sample-gathering box and weigh scale built in. Yield was then adjusted to 14% moisture content. Plot yields were weighed as harvested and a small sample collected for further analysis.

Variables examined in the trial included seed yield, test weight, plant height, and heading date. Samples of seed from each test plot were then packaged and sent to the University of Nebraska-Lincoln for oil analysis.

Results and Discussion

1.1 Camelina

Mean yield of this trial was 1,376 kg ha⁻¹ (Table 1). The highest yielding entry, at 1,711 kg ha⁻¹, was Calena. The lowest yielding entry, at 978 kg ha⁻¹, was NE Exp 684B. The moisture content averaged 7.6% for the 16 entries. The average test weight was 522 kg m⁻³. The average plant height was 77 cm. BSXG73 had the tallest height averaging 91 cm. The shortest entry was BSX-G52 averaging 63.5 cm. There were no significant differences in yield at the 95 percent probability level between the top 10 entries.

The mean total oil content was 29.5 percent. The entry BSX-G21 had the lowest percent oil content of 28.1 percent while the entry Calena had the highest oil content of 30.6 percent.

1.2 Canola

The mean yield of the 2006 trial was 1,680 kg ha⁻¹ (Table 2). The highest yielding entry, at 2,302 kg ha⁻¹, was Hyola 401. The lowest yielding entry, at 1,174 kg ha⁻¹, was Arid. The moisture content averaged 15.1% for the 18 entries. The average test weight was 590 kg m⁻³. The average plant height was 124 cm. 905 RR Hyclass had the tallest height averaging 142 cm. The shortest entry was Farmer averaging 42 107 cm. There were no significant differences in yield at the 95 percent probability level between the 18 entries.

The mean total oil content was 39.0 percent. The two brown mustard entries Arid and Dahinda, had the lowest percent oil content of 33.9 percent and 36.5 percent. The canola entry 905 RR Hyclass had the highest oil content of 41.6 percent. The mean stearic acid percent (C18:0) for all entries was 2.4. The mean oleic acid percent (C18:1) for all entries was 65.6.

Mean yield of the 2007 trial was 634 kg ha⁻¹. The highest yielding entry, at 1,251 kg ha⁻¹, was SW Marksman RR. The lowest yielding entry, at 341 kg ha⁻¹, was BSX 42078. The moisture content averaged 5.4 percent for the 22 entries. The average test weight was 494 kg m⁻³. The average plant height was 116 cm. Hilite 618CL had the tallest height of 132 cm. The shortest entry was 924 Hyclass RR at 99 cm.

The results shown of the 2007 trial are only one replication. Yields were very low in this trial and not all plots were harvested. High air temperatures during flowering and high numbers

of grasshoppers are possible reasons for the low yields. Statistical analysis could not be done with only one replication.

Based on the highest yielding line from the 2006 trial, gross crop income would be \$417 ha⁻¹ based on that year's contract price of \$0.24 kg⁻¹. These trials have not, however, included analysis of the costs of production that would potentially cut into the profit.

Summary

Hybrid poplar yields at ASC Farmington are very much in line with those observed in other parts of the country and around the globe. British experiments, which looked at tree spacing and biomass yield, saw production of 13.6 Mg ha⁻¹ yr⁻¹ (Armstrong, et al. 1999), and researchers in Minnesota have seen mean yields of 16 Mg ha⁻¹ yr⁻¹ (Riemenschneider 2001). In a 2003 study conducted by Oak Ridge National Laboratory (ORNL) 10 Mg ha⁻¹ yr⁻¹ was found to be the level above which biomass production was more profitable than the current land use system (Walsh, et al. 2003). With these yield targets from other regions, it appears that our top yielder (OP-367), and over half of the clones in the bioenergy trial, would be able to meet or exceed these values. While there are regional enterprises that could make use of hybrid poplar for wood products, however, there is not yet an infrastructure to handle wood as a source of potential ethanol feedstock.

Nebraska irrigated camelina trials from 2004 had a mean yield of 2,600 kg ha⁻¹, a bit greater than those observed at ASC Farmington. Irrigated spring canola trials in Nebraska (2005) had a mean yield of 1,222 kg ha⁻¹, slightly lower than those observed at ASC Farmington in 2006 (Nelson 2005). In the fall of 2007, a winter canola trial was established at ASC Farmington, and similar trials in Nebraska had a mean yield of 4,360 kg ha⁻¹. Based on the reduced yield of the 2007 spring canola trial, and pending results of the present winter canola study, it may appear that winter canola is a better fit with our short growing season and intense midsummer heat.

Both camelina and canola contain α -linolenic acid (ALA), an essential omega-3 (ω -3) fatty acid that cannot be synthesized in the human body and therefore must be obtained through food sources (see Tables 1 and 2 for oil content and fatty acid analysis). Though the mechanism is unclear, a weight of evidence shows that ALA can contribute to the prevention of coronary heart disease (Mozaffarian 2005) but may increase the risk of prostate cancer (Brouwer, et al. 2004). Nevertheless, the potential health benefits of ALA in food and food products underscore the tradeoffs involved when substituting food crops for fuel production.

Clearly, both hybrid poplar and oilseed crops can do well in our region, provided that irrigation water continues to be available and economic factors allow these crops a market footing in appropriate relation to those crops produced for feed or food. It will become increasingly important to balance the needs of food and other end-use products from our arid agricultural lands as costs for both food and fuel continue to rise. The development of a regional infrastructure to utilize these bioenergy crops will also play a huge role in shaping demand of bioenergy crops in our area and the arid Southwest as a whole.

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Table 1. Yield, moisture content at harvest, test weight, plant height, and oil content and fractionation of 16 varieties entered in the 2006 Camelina Variety Trial at the New Mexico State University Agricultural Science Center at Farmington, NM.

| Variety | Yield* (lb/acre) | Oil Content (%) | C18:0 Stearic (%) | C18:1 Oleic (%) | C18:2 Linoleic (%) | C18:3 Linolinic (%) | C20:0 Erucic (%) |
|----------------|-----------------------------------|--|--|--|---|--|---|
| Calena | 1712 | 30.6 | 2.6 | 14.5 | 19.3 | 35.7 | 2.3 |
| Ligena | 1683 | 29.5 | 2.6 | 16.0 | 21.3 | 34.7 | 2.3 |
| BSX-G72 | 1620 | 29.6 | 2.7 | 15.8 | 20.2 | 34.4 | 2.3 |
| BSX-G73 | 1571 | 30.1 | 2.7 | 15.6 | 20.6 | 33.9 | 2.3 |
| BSX-G63 | 1565 | 30.2 | 2.7 | 15.3 | 20.4 | 35.0 | 2.3 |
| BSX-G21 | 1539 | 28.1 | 2.6 | 15.9 | 19.3 | 35.7 | 2.1 |
| NE Exp 684 | 1455 | 30.3 | 2.7 | 15.6 | 21.0 | 35.1 | 2.3 |
| BSX-G62 | 1401 | 29.9 | 2.8 | 16.8 | 21.0 | 33.4 | 2.3 |
| NE Exp 682 | 1361 | 29.8 | 2.8 | 15.2 | 21.4 | 33.8 | 2.4 |
| BSX-G53 | 1349 | 29.4 | 2.8 | 14.7 | 20.3 | 35.3 | 2.4 |
| BSX-G51 | 1277 | 28.7 | 2.7 | 16.4 | 19.9 | 35.2 | 2.3 |
| BSX-G52 | 1199 | 30.3 | 2.4 | 15.7 | 18.9 | 36.8 | 2.1 |
| NE Exp 985 | 1146 | 29.1 | 2.6 | 15.6 | 19.5 | 35.8 | 2.2 |
| BSX-G61 | 1105 | 29.4 | 2.7 | 16.3 | 20.0 | 34.3 | 2.3 |
| BSX-G71 | 1052 | 28.8 | 2.8 | 15.9 | 20.9 | 33.9 | 2.4 |
| NE Exp 684B | 975 | 28.7 | 2.7 | 15.9 | 21.7 | 33.9 | 2.4 |
| Mean | 1375 | 29.5 | 2.7 | 15.7 | 20.4 | 34.8 | 2.3 |
| LSD (0.05) | 368.5 | 1.6 | 0.2 | 1.0 | 1.0 | 1.6 | 0.2 |
| CV (%) | 20.9 | 3.8 | 4.2 | 4.4 | 3.3 | 3.3 | 5.2 |
| P Value | 0.0067 | ns | 0.0006 | 0.0033 | <0.0001 | 0.0071 | 0.0137 |

*Yields were adjusted to 14% moisture content.

Table 2. Yield, moisture content at harvest, test weight, plant height, and oil content and fractionation of 16 varieties entered in the 2006 Brassica Variety Trial at the New Mexico State University Agricultural Science Center at Farmington, NM.

| Variety or Selection | Yield* (kg ha⁻¹) | Moisture Content (%) | Test Weight (lb/bu) | Plant Height (in) | Oil Content (%) | C18:0 Stearic (%) | C18:1 Oleic (%) | C18:3 Linolenic (%) |
|-----------------------------|--|---|--|--|--|--|--|--|
| Hyola 401 | 2302 | 13.0 | 607 | 109 | 39.3 | 2.6 | 66.9 | 7.5 |
| 905 RR Hyclas | 2189 | 15.8 | 581 | 142 | 41.6 | 2.3 | 64.9 | 7.8 |
| 431 RR Hyclas | 2055 | 14.0 | 593 | 130 | 40.3 | 2.5 | 65.5 | 7.5 |
| DKL 52-10 | 1946 | 14.7 | 609 | 140 | 38.8 | 2.2 | 64.7 | 7.8 |
| Hyola 357Mag.RR | 1931 | 13.5 | 593 | 109 | 38.8 | 2.7 | 66.6 | 7.0 |
| DKL 34-55 | 1769 | 14.0 | 600 | 122 | 40.4 | 2.6 | 65.4 | 6.7 |
| IS 7145 RR | 1754 | 15.6 | 588 | 119 | 40.1 | 2.2 | 69.6 | 7.4 |
| SW Patriot RR | 1743 | 15.2 | 599 | 127 | 39.8 | 2.3 | 65.2 | 7.7 |
| Farmer | 1689 | 13.3 | 586 | 107 | 37.9 | 2.5 | 65.8 | 7.3 |
| DKL 38-25 | 1677 | 15.1 | 602 | 135 | 39.8 | 2.1 | 64.3 | 8.0 |
| 767 SWRR Hyclas | 1585 | 15.7 | 604 | 132 | 39.3 | 2.3 | 65.1 | 7.7 |
| IS 3465 RR | 1516 | 14.2 | 602 | 124 | 38.8 | 2.5 | 66.2 | 6.7 |
| Hylite 1618 CL | 1496 | 16.2 | 591 | 132 | 39.3 | 2.4 | 65.0 | 7.6 |
| 712 RR Hyclas | 1466 | 16.0 | 591 | 122 | 40.1 | 2.3 | 68.1 | 7.2 |
| Dahinda (brown mustard) | 1414 | 14.8 | 576 | 124 | 36.5 | 2.4 | 64.7 | 8.1 |
| SW Marksman RR | 1296 | 15.7 | 577 | 127 | 38.3 | 2.3 | 66.1 | 8.0 |
| SW Titan RR | 1245 | 16.2 | 594 | 122 | 38.3 | 2.4 | 64.4 | 7.3 |
| Arid (brown mustard) | 1174 | 18.2 | 527 | 117 | 33.9 | 2.4 | 62.2 | 8.2 |
| Mean | 1680 | 15.1 | 590 | 124 | 39.0 | 2.4 | 65.6 | 7.5 |
| LSD (0.05) | ns | 2.0 | 27 | ns | 1.8 | 0.2 | 3.2 | † |
| CV (%) | 29.1 | 9.2 | 3.2 | 12 | 3.2 | 5.7 | 3.4 | † |
| P Value | 0.0762 | 0.0003 | <0.0001 | 0.0682 | <0.0001 | <0.0001 | 0.0290 | † |

*Yields were adjusted to 14% moisture content.

†Analysis not complete due to loss of replicate values.

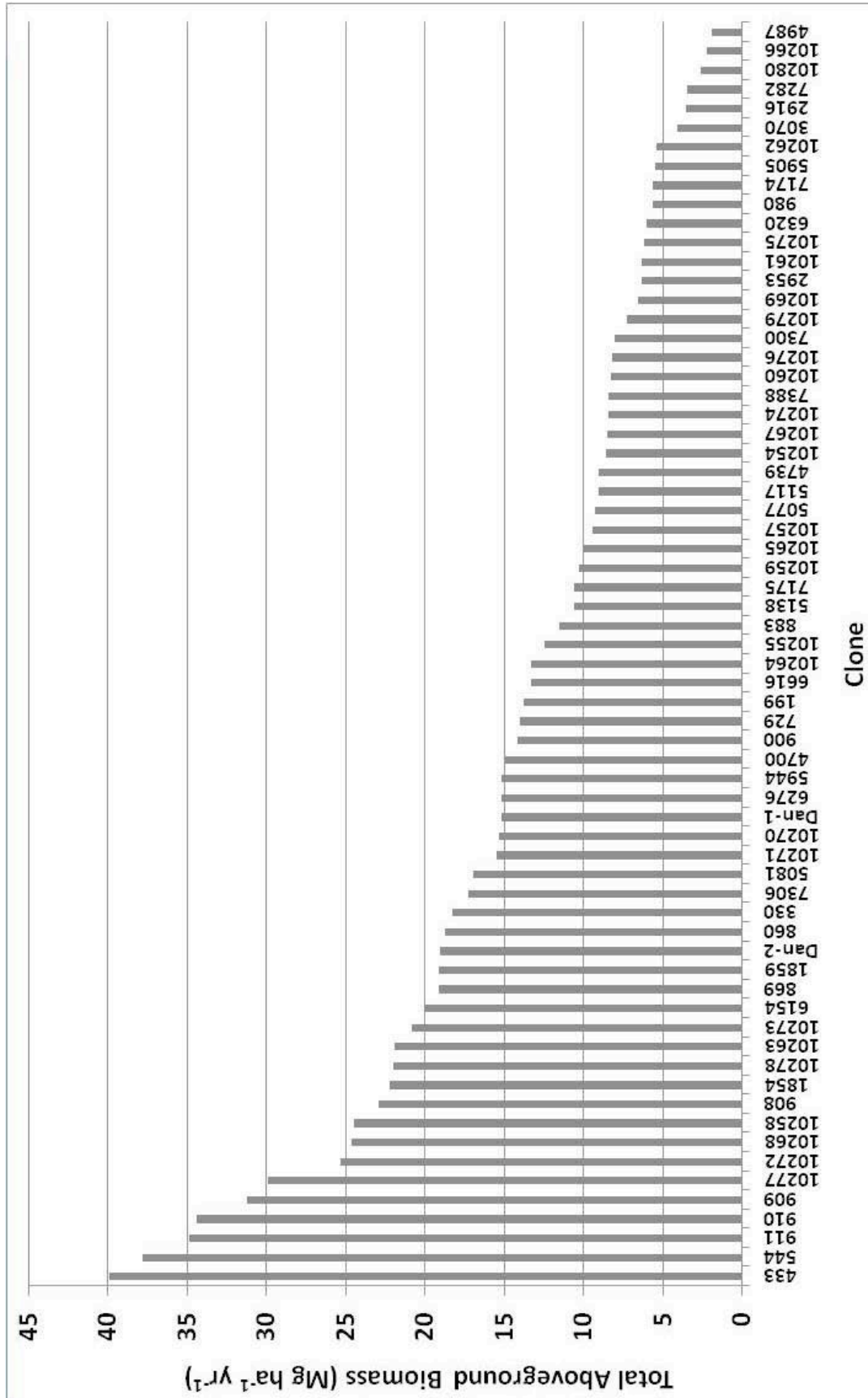


Figure 1. Total aboveground biomass (TAB) for 66 clones entered in hybrid poplar trial established in 2005 at the New Mexico State University Agricultural Science Center at Farmington, NM. Results are in mean annual biomass increment ($\text{Mg ha}^{-1} \text{ yr}^{-1}$) calculated on the third year of the trial. Mean TAB was $14.6 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ and ORNL estimate of feasibility occurs at $10 \text{ Mg ha}^{-1} \text{ yr}^{-1}$. Trial will be harvested after year five.

