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High-sulfur Coal Desulfurization for Oxyfuels

Richard D. Doctor and Dr. John C. Molburg

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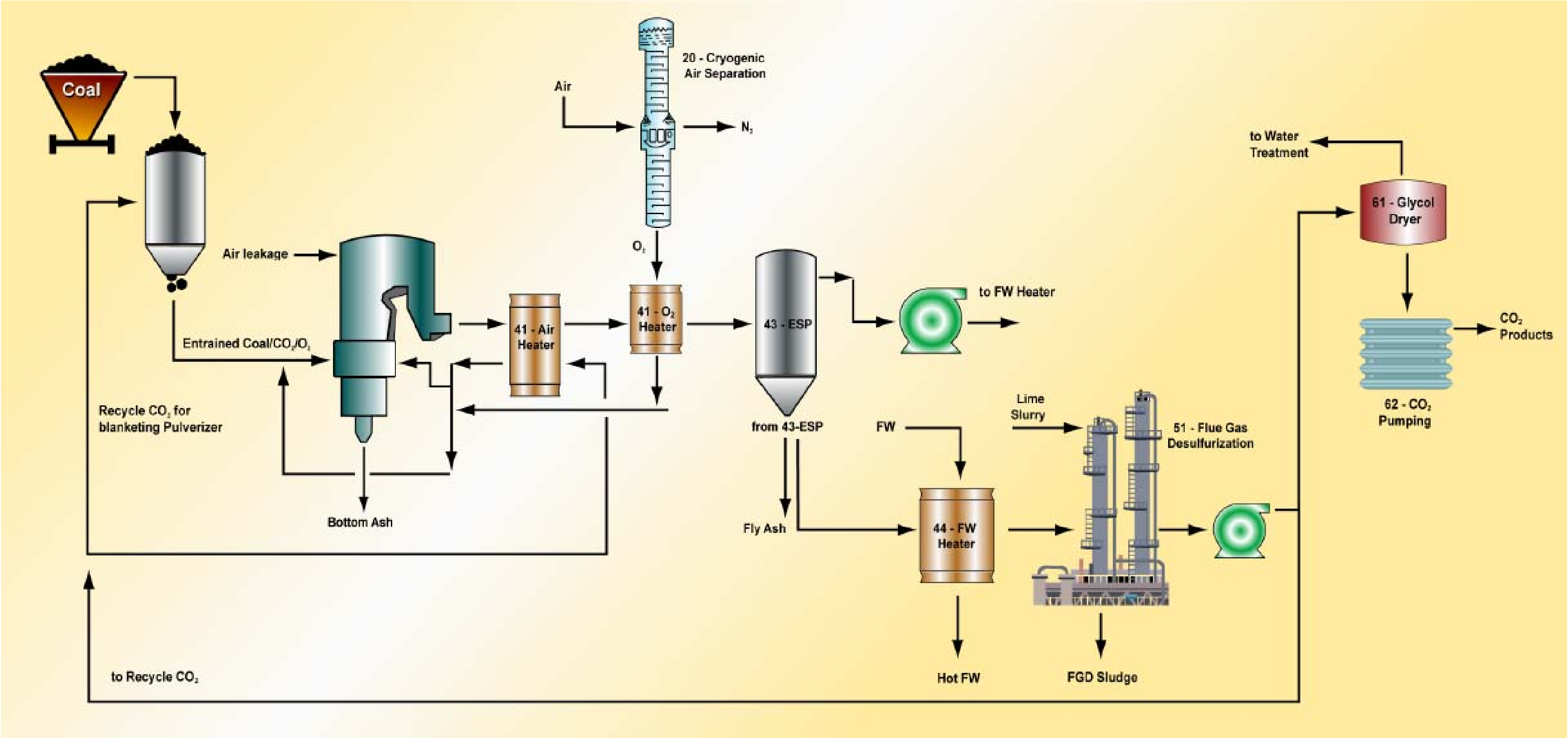
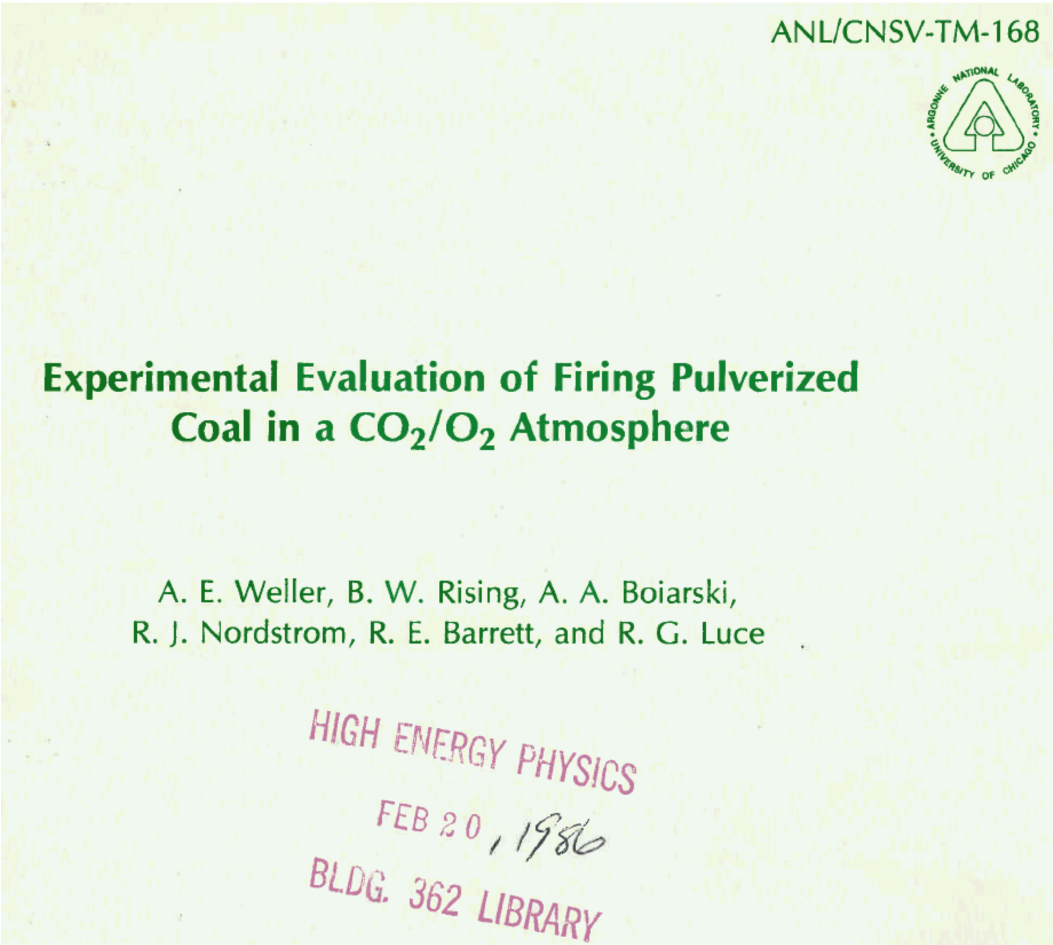
CO_2 Capture for PC-Boilers using Oxy-Fuels – a Transitional Strategy



In 1985 Argonne initiated research on retrofitting boilers with flue gas recirculation (O_2-firing or Oxy-fuels) for CO_2 capture. This positions power stations for later repowering to IGCC since unlike other CO_2 capture major equipment such as Air-separation, CO_2 pumps and CO_2 pipelines transition nicely into a higher MW capacity IGCC retrofit.

Experimental Studies on firing Coal a CO_2/O_2 Atmosphere initiated work on Oxyfuels (October 1985)

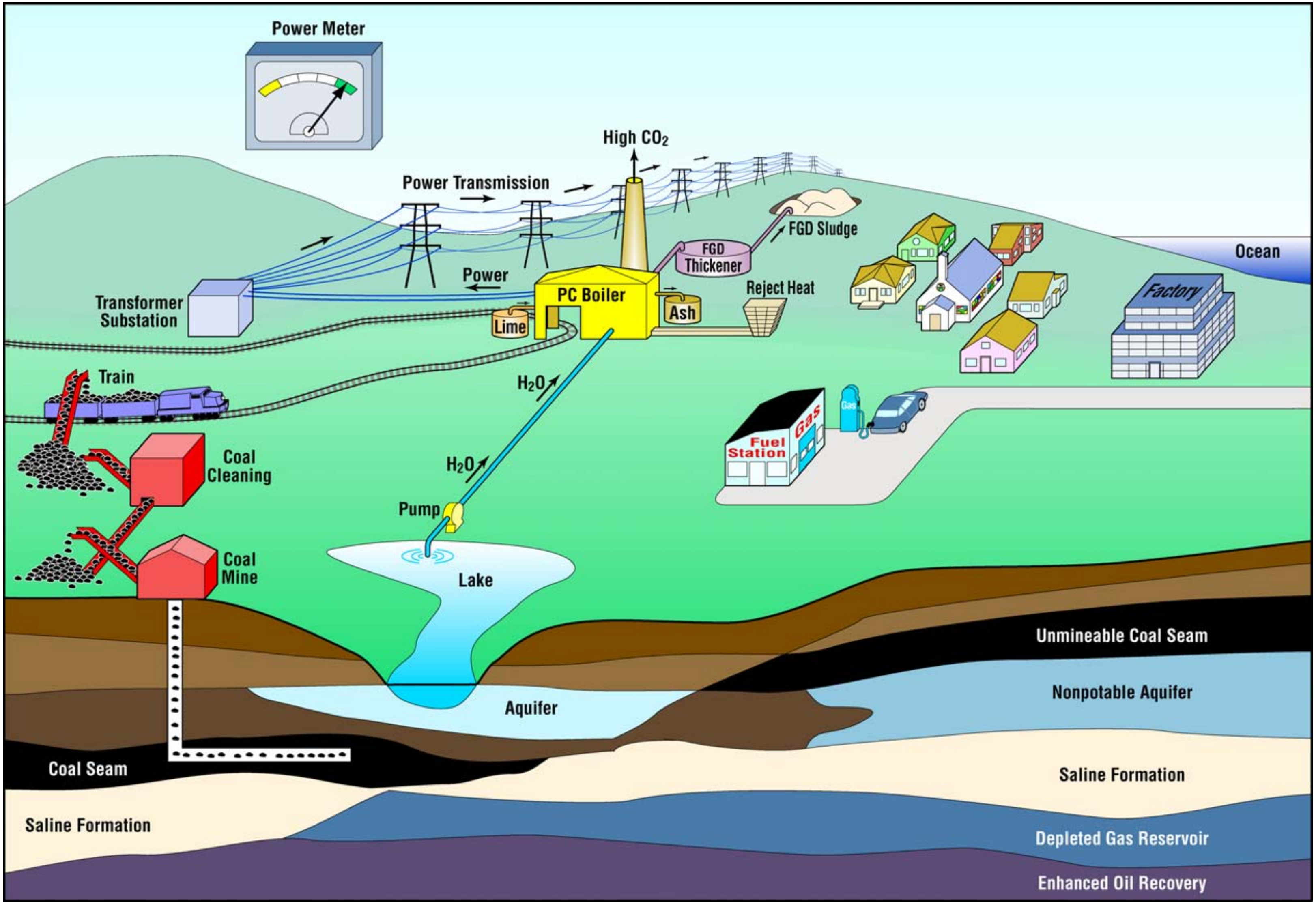

ANL/CNSV-TM-168

Experimental Evaluation of Firing Pulverized Coal in a CO_2/O_2 Atmosphere

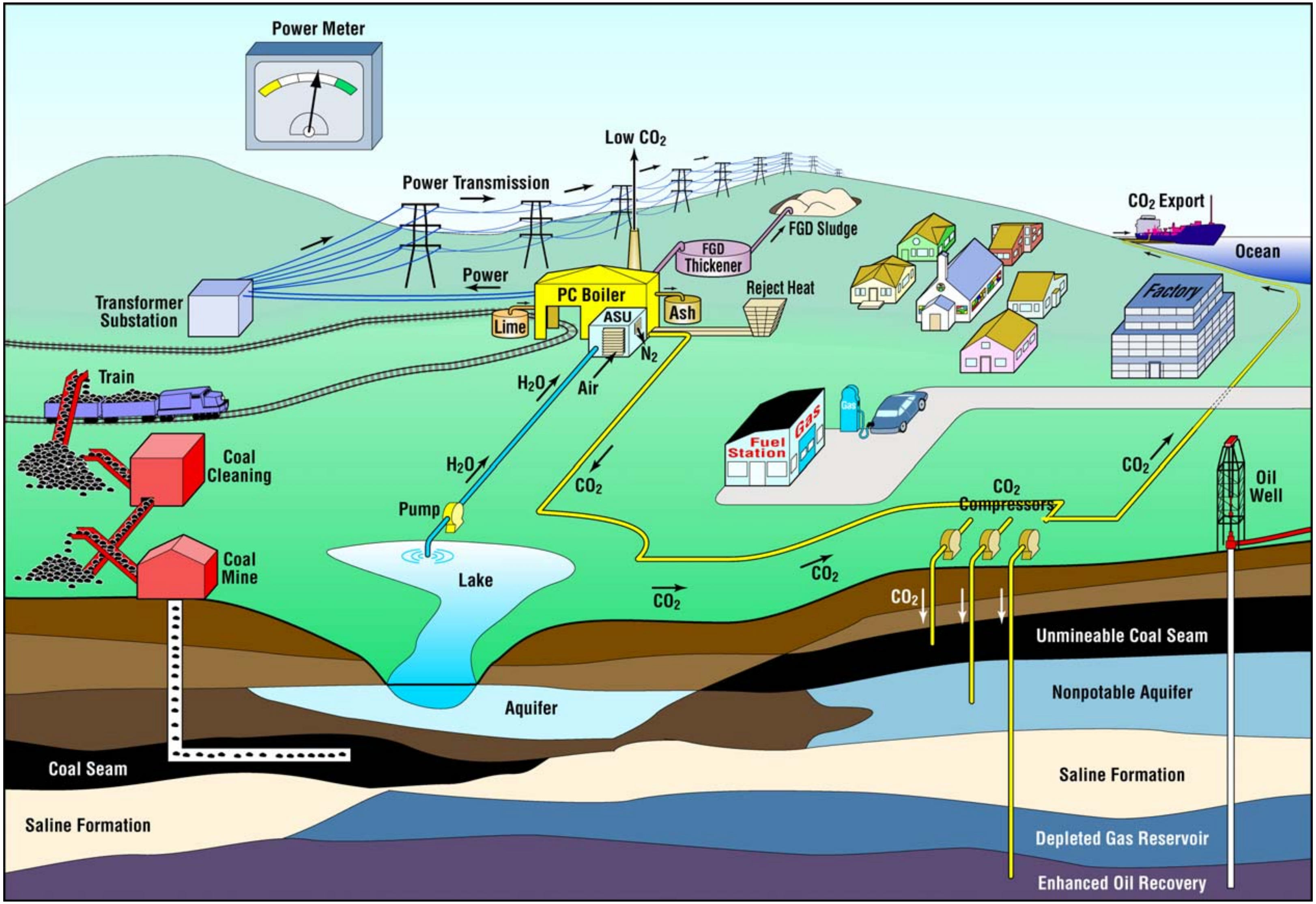
A. E. Weller, B. W. Rising, A. A. Boiarski, R. J. Nordstrom, R. E. Barrett, and R. G. Luce

"….a new method being investigated by Argonne, of recovering carbon dioxide that now escapes from smokestacks; this method would avoid the emissions of sulfur oxides and nitrous oxides believed to be precursors to acid rain. Studies of use options relate primarily to increased exploitation of carbon dioxide for enhanced oil recovery."

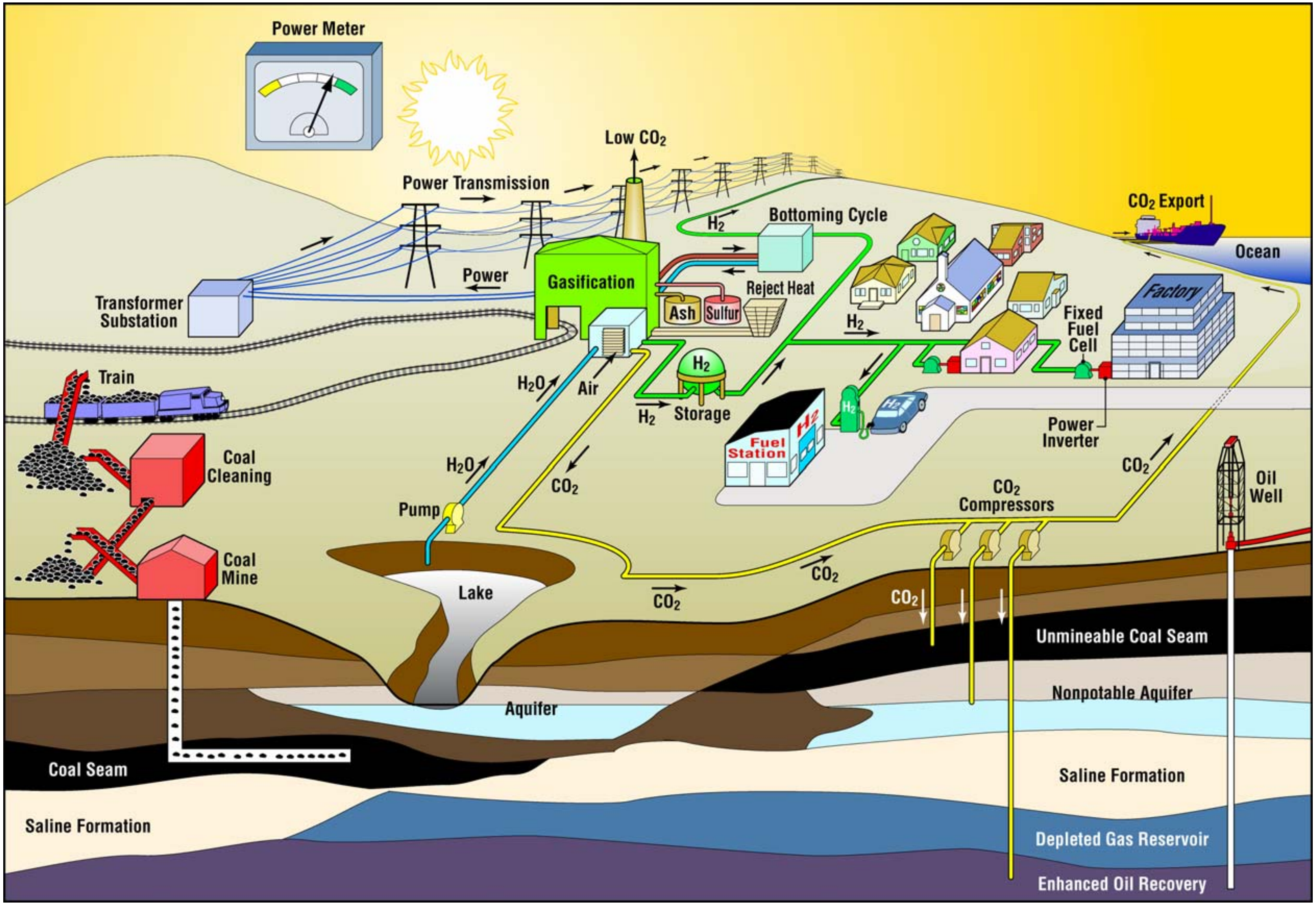
Pulverized Coal-fired Boiler



Pulverized Coal-fired Boiler – retrofitted for low CO_2



Water use in power cycles may require novel approaches



Site-specific Oxyfuel vs. Amine retrofit; 300 MW

Doctor, Molburg, et al, "CO2 Capture for PC-Boilers Using OXY-FUELS – A Transition Strategy," GHGT-7 (Sept. 2004)

Green highlights – equipment that retrofits for IGCC repowering

	Oxy-fuel	Amine (MEA)
Air Separation Unit	$101,000	
Amine Scrubber		$67,992
Ducts/Dampers/Air heaters/Controls	$2,571	$1,697
Feed water Heater	$395	
O2 Heater	$193	
Seal Boiler for 1% in-leakage	$22	
Cooling Towers/Cooling Pumps		$35,790
Flue Gas Desulfurization/Caustic	$6,317	$8,423
Chemical Treatment		$8,949
CO2 Conditioning and Compression	$36,828	$33,145
TOTAL DIRECT COSTS	*$147,326*	*$155,995*
RETROFIT CAPABLE for IGCC	*$137,828*	*$68,935*

Types of CO_2 impurities that need to be managed

- Free Water – corrosion; hydrates
- Oxygen – corrosion
- SO_2 – corrosion/safety
- SO_3 – should be removed within capture
- NO; NO_2 – corrosion
- HCl – should be removed within capture
- H_2S – corrosion, cost, environment restrictions, changes risk, toxicity
- Nitrogen, Argon – diluents, design for 2-phase conditions
- CH_4 in natural gas

CO_2 Pipeline Specification will drive design
Acid gas experience shows that up to 45% H_2S is practical

U.S. Quality Specifications for CO_2 – KinderMorgan

CO_2	95%	Min	MMP Concern
Nitrogen	4%	Max	MMP Concern
Hydrocarbons	5%	Max	MMP Concern
Water	30 lbs/MMcf	Max	Corrosion
Oxygen	10 ppm	Max	Corrosion
H_2S (Sulfur)	10 – 200 ppm	Max	Safety
Glycol	0.3 gal/MMcf	Max	Operations
Temperature	120 deg F	Max	Materials

- **MMP – minimum miscibility pressure for EOR use only**

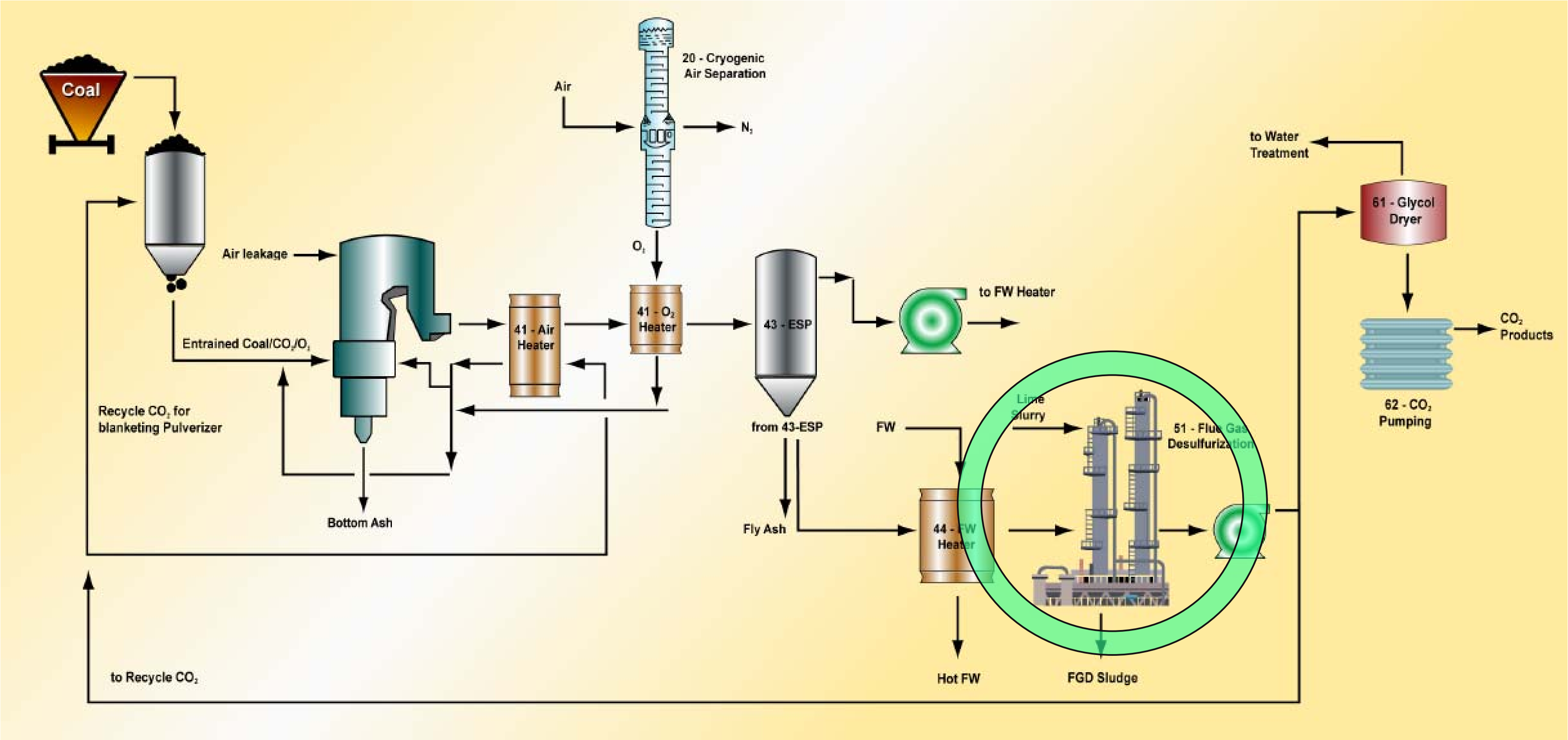
CO_2 Pipeline Specifications — DOE

Carbon dioxide (CO_2), whether being sold for chemical processing or being seque
supplied as a liquid and must meet the pipeline specification shown in Table 4 (Bock et al, 2002:

Table 4. Carbon Dioxide Pipeline Specification	
Pressure	152 bar
Water Content	233 K (-40 °F) dew point
N_2	<300 ppmv
O_2	< 40 ppmv
Ar	<10 ppmv

<u>Quality Guidelines for Energy System Studies,</u> **Office of Systems and Policy Support, Gilbert V. McGurl, Robert E. James, Edward L. Parsons, John A. Ruether, John G. Wimer (February 2004)**

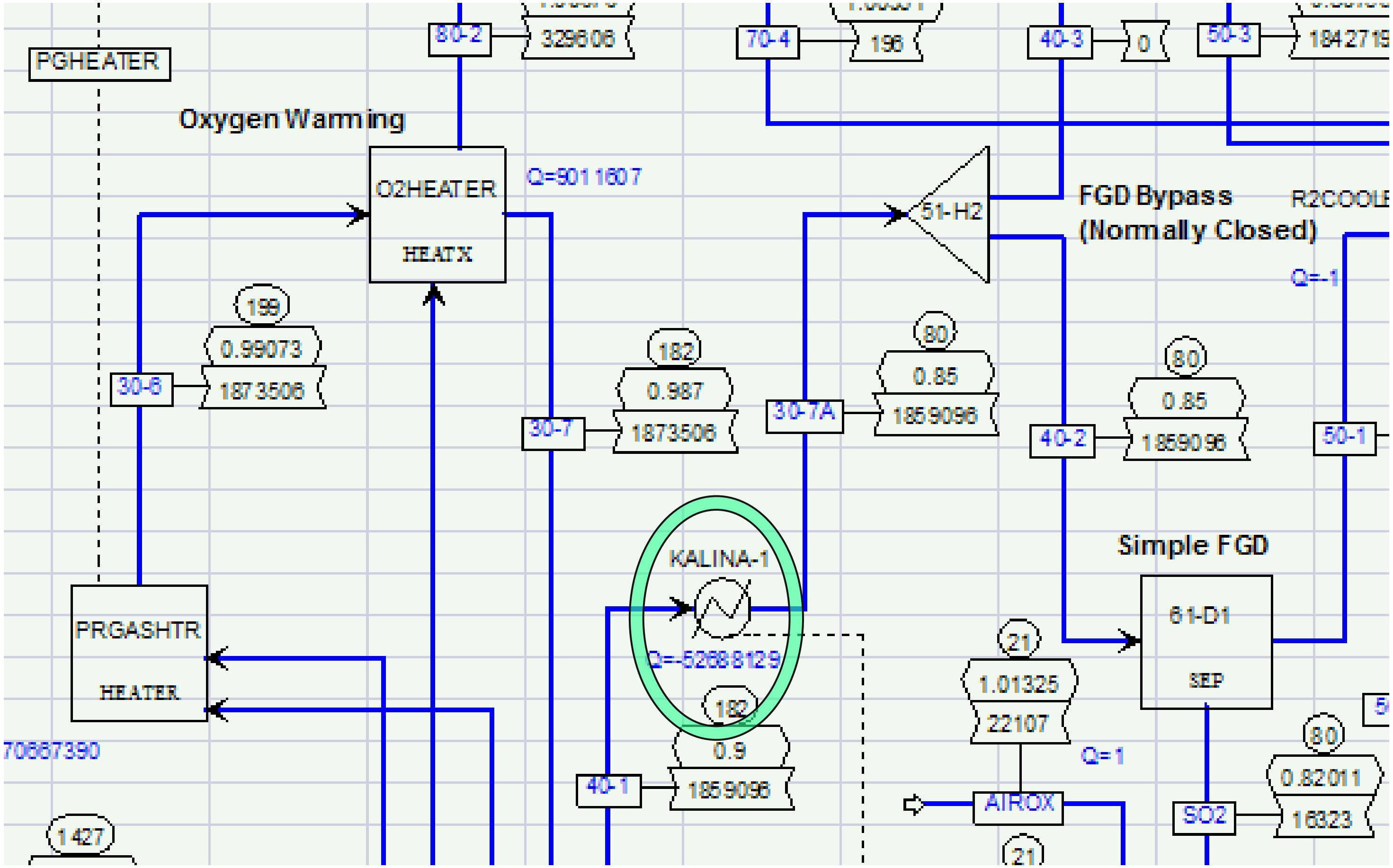
Retrofit to existing boilers for CO_2 capture
This talk will focus on the FGD system



Oxyfuels has studied 3 coals – This work focuses on IL #6 with 4.84% sulfur

	Illinois # 6	Upper Freeport	Wyodak
HHV (Btu/lb)	10,999	13,315	8,426
Ultimate Analysis from NETL Guidelines, Table 2			
Moisture	***7.97%***	***1.13%***	***28.09%***
Carbon	60.42%	73.39%	49.21%
Hydrogen	3.89%	4.03%	3.51%
Nitrogen	1.07%	1.33%	0.73%
Chlorine	0.05%	0.00%	0.02%
Sulfur	4.45%	2.29%	0.45%
Ash	14.25%	13.03%	6.31%
Oxygen	7.90%	4.80%	11.68%
Sulfur Analysis			
Pyritic	2.40%	1.20%	0.20%
Sulfate	0.04%	0.02%	0.03%
Organic	2.40%	1.10%	0.40%

System performance improves by transferring 52.7 MW of process heat after the bag house & before FGD to Kalina cycle chilling



Oxyfuels require considerable chilling that may be supplied by Bottoming cycles — they reclaim waste heat while delivering chilling

- Ammonia bottoming cycle with air-cooled condenser, could use a mixture organic working fluids to maximize conversion from waste heat sources such as turbine exhaust and stack gas.
- An optimized mixture of working fluids, with varying boiling points (Kalina cycles) overcomes the limitation of the Rankine cycle based on constant temperature boiling of single component.
- Thermo-electric conversion historically has been limited by materials.

Source: Energy Concepts, Annapolis, MD

Current applications of chiller and bottoming cycles in refinery service

Ocean Thermal Energy Conversion can deliver power and hydrogen from off-shore oil platforms sitting on depleted fields

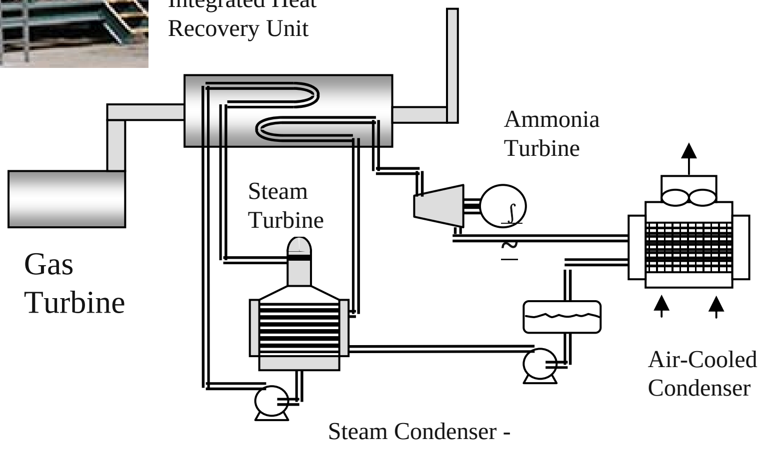
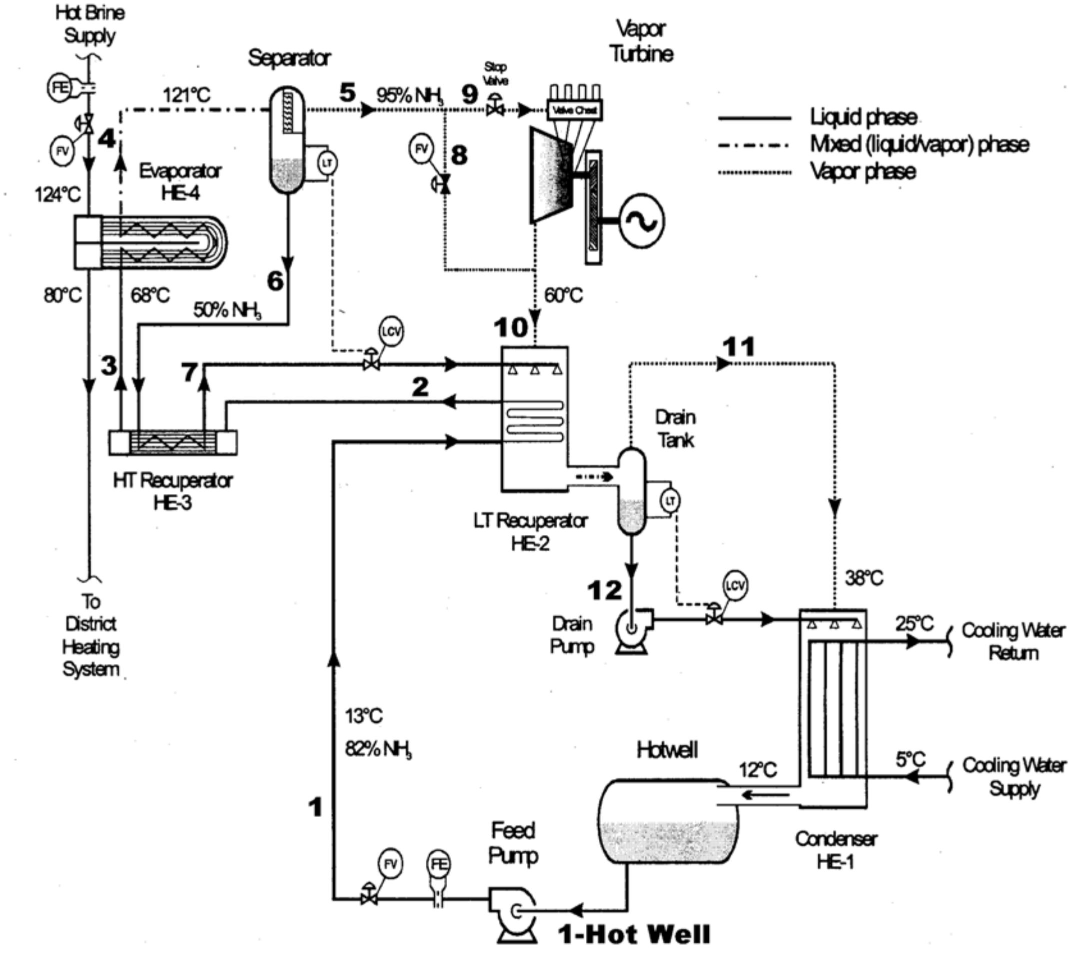


Figure 1. Ammonia bottoming cycle to GTCC with air-cooled condenser.

Simulation to validate Kalina

(OMMI Vol. 1, Issue 2; August 2002; "Testing and Operating Experience of the 2 MW Kalina Cycle Geothermal Power Plant in Húsavík, Iceland," Mirolli)



Kalina cycle chilling

- This cycle was reviewed using an ASPEN 20 simulation so that we could better understand the conditions. The working fluid electrolyte properties (82% Ammonia – 18% Water; 10 tonnes/h) were considered since this is critical to process predictions.
- In Iceland, a geothermal brine supplies 2.5 MW of input heat and two turbine stages were employed yielding 294 kW, for a conversion efficiency of 11.8%. The turbine design and bypass were designed so that the steam quality would be no lower than 98% at the exit of each stage.
- The working fluid's bubble point is ~17 C, with -5 C sub-cooling to the high pressure pump inlet (12 C feed at 5.4 bar). Redesign of the system to accommodate local ambient conditions would put the ammonia-water ratio closer to 1:1.
- In the 90-20 C operating range, 4 C chilling can be obtained with an efficiency of 0.6-kW for every 1-kW of input.

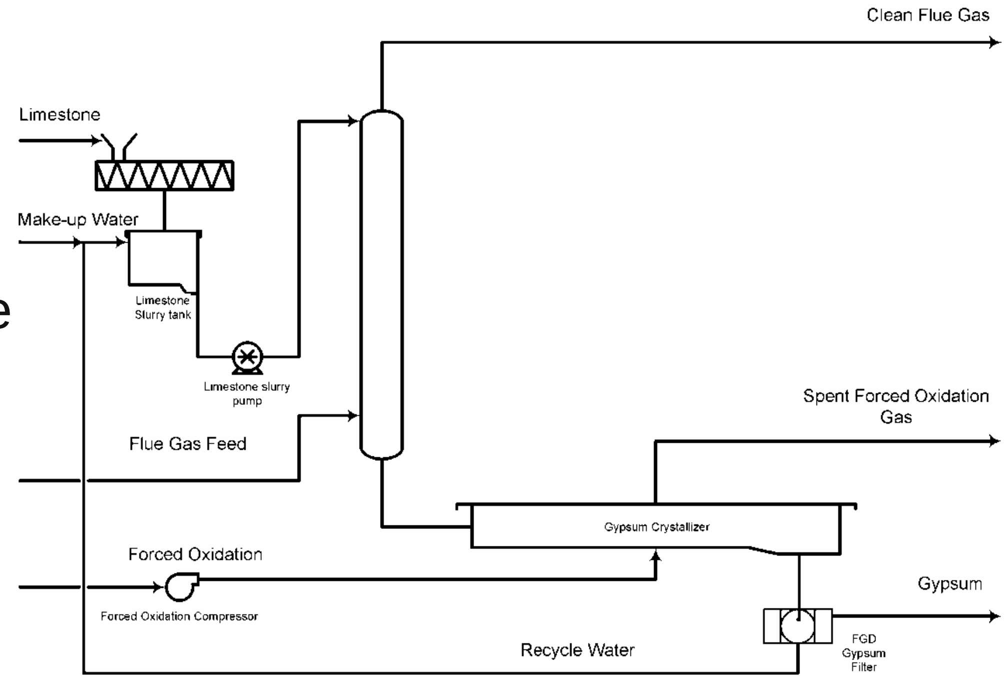
Comparison of Air vs. Oxyfuels flue gas to sulfur control

Mole fraction	Air	Oxyfuel	
H_2O	6.81%	11.97%	
N_2	75.99%	1.55%	
O_2	2.86%	3.48%	
CO_2	13.86%	82.36%	
CO	7.885E-05	0.000478	
HCl	3.571E-05	5.4E-05	
SO_2	3.82E-03	5.77E-03	146,064 kg/hr
NO	7.83E-04	1.09E-04	
Total Flow (kmol/hr)	6.72E+04	4.61E+04	46%
Total Flow (kg/hr)	2.00E+06	1.86E+06	8%
Total Flow (m^3/hr)	2.32E+06	1.59E+06	46%
Temperature (^oC)	80	80	
Pressure (bar)	0.85	0.85	

Because the flow rates with air are higher, the FGD contacting tower capital is higher

For the FGD Key electrolytes were considered

To prevent Nitrogen from infiltrating the desulfurized product gas, the ASPEN suite was run with the electrolyte suite feature and the Forced Oxidation system now employs Oxygen mixed with an Oxy-fuel-derived CO_2 stream.



Reaction	Type	Stoichiometry
1	Equilibrium	2 H2O <--> H3O+ + OH-
2	Equilibrium	CO2 + 2 H2O <--> H3O+ + HCO3-
3	Equilibrium	HCO3- + H2O <--> H3O+ + CO3--
4	Equilibrium	SO2 + 2 H2O <--> H3O+ + HSO3-
5	Equilibrium	HSO3- + H2O <--> H3O+ + SO3--
6	Equilibrium	CAOH+ <--> CA++ + OH-
CASO3(S)	Salt	CASO3(S) <--> CA++ + SO3--
CASO3*HM	Salt	CASO3*HM <--> CA++ + SO3-- + 0.5 H2O
CA(OH)2	Salt	CA(OH)2 <--> CAOH+ + OH-
CACO3(S)	Salt	CACO3(S) <--> CA++ + CO3--

Comparison – same sulfur loading, with constant mole flow

- For the same molar gas feed rate (conventional which actually is 46% higher and Oxyfuels) with the same sulfur loading
- There are some striking contrasts on the carbonate-related electrolytes.

	FLUE GAS FEED	
	Air	Oxyfuel
Temperature F	283	283
Pressure psi	14.7	14.7
Vapor Frac	1	1
Solid Frac	0	0
Mole Flow lbmol/hr	1.00E+05	1.00E+05
Mass Flow lb/hr	2.94E+06	4.18E+06
Volume Flow cuft/hr	5.42E+07	5.41E+07
Enthalpy MMBtu/hr	-2.89E+03	-1.56E+04
Mass Flow lb/hr		
O2	160,798	111,996
N2	2,055,260	14,007
CO2	530,772	3,899,270
SO2	32,193	32,193
H2O	162,952	124,260
CA++	0	0
CAOH+	0	0
H3O+	0	0
OH-	0	0
HCO3-	0	0
HSO3-	0	0
HSO4-	0	0
CO3--	0	0
SO3--	0	0
SO4--	0	0
CACO3(S)	0	0
CASO3*HM	0	0
CASO4*HM	0	0
CASO4*2	0	0

With Oxyfuels water use goes up by 14%

Photo: PG&E Water filters

	LIMESTONE SLURRY	
	Air	Oxyfuel
Temperature F	90	90
Pressure psi	14.7	14.7
Vapor Frac	0	0
Solid Frac	0.046	0.039
Mole Flow lbmol/hr	1.27E+04	1.49E+04
Mass Flow lb/hr	2.76E+05	3.17E+05
Volume Flow cuft/hr	3.85E+03	4.51E+03
Enthalpy MMBtu/hr	-1.78E+03	-2.06E+03
Mass Flow lb/hr		
O2	0	0
N2	0	0
CO2	0.0003	0.0004
SO2	0	0
H2O	218,000	258,710
CA++	1.24	1.47
CAOH+	0.0039	0.0046
H3O+	0	0
OH-	0.3904	0.4633
HCO3-	1.40	1.67
HSO3-	0	0
HSO4-	0	0
CO3--	0.4787	0.5681
SO3--	0	0
SO4--	0	0
CACO3(S)	57,836	57,835
CASO3*HM	0	0
CASO4*HM	0	0
CASO4*2	0	0

Forced Oxidation for high sulfur removal rates 98% and higher is established industrial practice

Table 7. Additional Design Parameters Used for Wet FGD Comparison

	LSFO	MEL
SO_2 removal, %	98%	98%
By product	Gypsum	Gypsum
Reagent	Limestone	Lime
Reagent cost, $/ton	15	50
Reagent purity, %	95	94
Reagent ratio, moles of reagent/mole of sulfur removal	1.03	1.02
SO_2 oxidation stoichiometry (moles O fed/mole SO_2 removed)	3.0	3.0

DePriest, William and Rajendra P. Gaikwad, Sargent & Lundy LLC, "Economics of Lime and Limestone for Control of Sulfur Dioxide," Combined Power Plant Air-Pollutant Control Symposium, AWMA, Washington, DC (May 19-22, 2003).

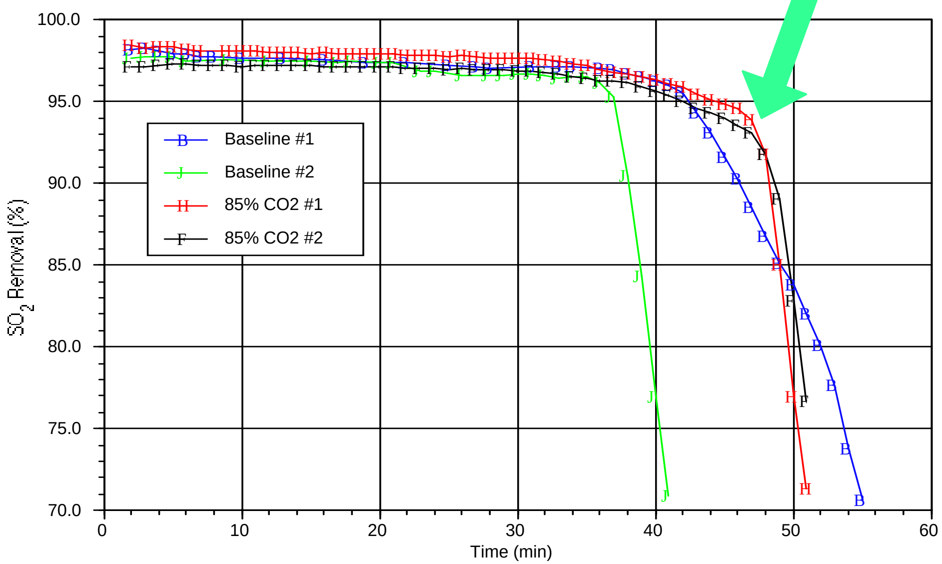
Recovery of sulfur must be as Gypsum [$Ca(SO_4)\cdot 2H_2O$]

- The Oxygen use for both systems comes to 2.2 tonnes/hr
- For the Oxyfuels assuming O_2 costs ~$25/tonne there is an incentive to see how far enrichment can be pursued without N_2 in-leaking costing more
- The FGD system benefits the Oxyfuels by accomplishing significant drying – spent oxidation gas is returned to boiler

	FORCED OXIDATION		SPENT F-OX GAS	
	Air	Oxyfuel	Air	Oxyfuel
Temperature F	140	140	90	90
Pressure psi	14.7	14.7	14.7	14.7
Vapor Frac	1	1	1	1
Solid Frac	0	0	0	0
Mole Flow lbmol/hr	7.18E+03	8.42E+03	7.00E+03	8.23E+03
Mass Flow lb/hr	2.07E+05	3.23E+05	2.03E+05	3.05E+05
Volume Flow cuft/hr	3.14E+06	3.67E+06	2.81E+06	2.78E+06
Enthalpy MMBtu/hr	3.14E+00	-1.09E+03	-3.71E+01	-1.00E+03
Mass Flow lb/hr				
O2	48,239	48,238	43,419	43,419
N2	158,870	820	158,870	820
CO2	0	254,429	16	254,429
SO2	0	0	0	0
H2O	168	19,775	336	6,053
CA++	0	0	0	0
CAOH+	0	0	0	0
H3O+	0	0	0	0
OH-	0	0	0	0
HCO3-	0	0	0	0
HSO3-	0	0	0	0
HSO4-	0	0	0	0
CO3--	0	0	0	0
SO3--	0	0	0	0
SO4--	0	0	0	0
CACO3(S)	0	0	0	0
CASO3*HM	0	0	0	0
CASO4*HM	0	0	0	0
CASO4*2	0	0	0	0

The crystallizer feed shows higher Ca^{++} consistent with experiments in our laboratory there is better sorbent utilization

Oxyfuels benefit lime FGD use



Mendelsohn, M.H., and R.D. Doctor, *"Aqueous Scrubber Performance Using a High Concentration of Carbon Dioxide (CO2) in a Simulated Flue Gas Stream,"* (June 2001)

	CRYSTALLIZER FEED	
	Air	Oxyfuel
Temperature F	130	130
Pressure psi	14.7	14.7
Vapor Frac	0	0
Solid Frac	0.011	0.011
Mole Flow lbmol/hr	7.64E+04	7.64E+04
Mass Flow lb/hr	1.47E+06	1.47E+06
Volume Flow cuft/hr	2.25E+04	2.26E+04
Enthalpy MMBtu/hr	-9.71E+03	-9.71E+03
Mass Flow lb/hr		
O2	1.85	1.26
N2	13	8.61E-02
CO2	125	867
SO2	5.00E-04	3.40E-03
H2O	1,360,540	1,359,430
CA++	891	985
CAOH+	3.20E-03	1.30E-03
H3O+	1.44E-02	3.96E-02
OH-	4.70E-03	1.70E-03
HCO3-	266	675
HSO3-	13	32
HSO4-	1.10E-01	2.80E-01
CO3--	8.50E-02	8.02E-02
SO3--	2.0	1.9
SO4--	1,916	1,809
CACO3(S)	16,938	17,281
CASO3*HM	88,319	88,322
CASO4*HM	0	0
CASO4*2	2,650	2,393

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Gypsum recovery – dewatering is going to be critical

Because of the different chemical environment, it should be possible to grow gypsum, but kinetics and crystal morphology need experimental confirmation

Source: *Science* — March 7, 2008

	GYPSUM	
	Air	Oxyfuel
Temperature F	90	90
Pressure psi	14.7	14.7
Vapor Frac	0	0
Solid Frac	0.123	0.122
Mole Flow lbmol/hr	4.70E+03	4.72E+03
Mass Flow lb/hr	1.59E+05	1.60E+05
Volume Flow cuft/hr	1.48E+03	1.49E+03
Enthalpy MMBtu/hr	-9.20E+02	-9.21E+02
Mass Flow lb/hr		
O2	3.75E-01	3.42E-01
N2	9.94E-01	5.20E-03
CO2	2.12E-01	7.63E+01
SO2	0	0
H2O	74,292	74,498
CA++	47	60
CAOH+	3.00E-04	0.00E+00
H3O+	1.00E-04	1.90E-03
OH-	5.00E-04	0.00E+00
HCO3-	3.55	61.82
HSO3-	8.77E-02	1.53E+00
HSO4-	4.00E-04	6.50E-03
CO3--	7.40E-03	6.40E-03
SO3--	1.56E-01	1.35E-01
SO4--	109	95
CACO3(S)	8,548	8,455
CASO3*HM	24,734	24,732
CASO4*HM	0	0
CASO4*2	51,620	51,640

Flue gas clean-up with good contacting delivers SO_2 < 100 ppm

- Some pipeline standards have argued for further polishing

Photo: Kinder Morgan

	CLEAN FLUE GAS	
	Air	Oxyfuel
Temperature F	132.9	132.9
Pressure psi	14.7	14.7
Vapor Frac	1	1
Solid Frac	0	0
Mole Flow lbmol/hr	1.07E+05	1.10E+05
Mass Flow lb/hr	3.06E+06	4.35E+06
Volume Flow cuft/hr	4.63E+07	4.73E+07
Enthalpy MMBtu/hr	-3.77E+03	-1.68E+04
Mass Flow lb/hr		
O2	160,803	112,000
N2	2,055,260	14,007
CO2	552,246	3,921,520
SO2	644	644
H2O	292,484	299,225
CA++	0	0
CAOH+	0	0
H3O+	0	0
OH-	0	0
HCO3-	0	0
HSO3-	0	0
HSO4-	0	0
CO3--	0	0
SO3--	0	0
SO4--	0	0
CACO3(S)	0	0
CASO3*HM	0	0
CASO4*HM	0	0
CASO4*2	0	0

Oxyfuels – Economic impacts

- For a 450 MW Oxyfuel boiler burning High-sulfur IL#6 coal the additional FGD oxygen demands increase total oxygen consumption at the plant from 358 tonnes/h to 360 tonnes/h
- The cost of electricity will be impacted by the Flue Gas Desulfurization by ~5 mills/kWh

Oxyfuels FGD Operating Costs

PERFORMANCE					Gross power heat rate HHV (Btu/kWh)	10,000
					Gross power heat rate HHV (kJ/kWh)	10.56
	Operating hours per year		7,709		Capacity factor	88.00%
					Annual Net Power Production (MW)	3,627,923
Consumables						
	Oxygen (99% purity)	2	tonne/h	$25.00	$/tonne	$254
	Ash and FGD sludge disposal	80	tonne/h	$15.00	$/tonne	$9,229
	Limestone	28.9	tonne/h	$15.00	$/tonne	$3,344
	Other chemicals, dessicant, compressor oil					$73
Plant Labor	Operations (w benefits)	3.5	men/shift	$28.00	$/h	$858
	Supervision/support	25%	of above			$215
Maintenance						
	CO_2 Capture	2.0%	@	$16	$/kW	$152
Utilities						
	Flue Gas Desulfurization	3.1	MW	$50.00	$/MWh	$1,187
	Natural Gas and other utilities	0	10^6 Btu/h	$5.00	$/$10^6$ Btu	$0
	ConsumptiveWater	432.00	gpm	$71.00	$/gpm/yr	$31
Other	Insurance & Local Taxes	0.9%	of Direct + Base			$1,716
	Other - % of Operations labor	12.5%	of above			$134
NET OPERATING COSTS						***$17,192***

FGD Costs for CO_2 will be ~5 mills/kWh

SUMMARY OF COSTS	**Air**		**Oxyfuels**	
Cost of Electricity - Levelized	mills/kWh		mills/kWh	
Capital Charge	0.38		0.29	
Operating & Maintenance	4.69		4.74	
Costs after plant fence	0.00		0.00	
BUSBAR COST OF ELECTRICITY	**5.07**	**mills/kWh**	**5.03**	**mills/kWh**

Conclusions – Cost impacts for FGD ~ 5mills/kWh

- For the same molar feed rate of gas from conventional and Oxyfuels, with the same sulfur loading on a weight basis the Crystallizer Feed (the FGD Scrubber bottoms liquor) shows some *striking contrasts on the carbonate-related electrolytes*.
- It is believed that this approach supports the technical feasibility of retrofitting PC-boilers for sulfur control to protect the CO_2-pipeline and injection reservoir where gypsum formation must be avoided and there are safety concerns *– Experimental validation is needed*
- *Waste heat recovery to provide chilling* should be pursued
- Oxyfuel FGD will have a modest impact on water consumption ~14% compared to conventional FGD
- Forced oxidation off-gas can be integrated into the process
- The Oxygen use for both systems comes to 2.2 tonnes/hr
- For the Oxyfuels assuming O_2 costs ~$25/tonne there is an incentive to see how far enrichment can be pursued without N_2 in-leaking costing more – *cost impacts ~0.12 mills/kWh*

My mail last week – IPCC Nobel Peace Prize Certificate