Lecture 5:

Oxy-Pulverised Coal Combustion Technology for Power Generation with CO_2 Capture (Engineering Principles)

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2nd APP Oxyfuel Working Group Capacity Building Course

Beijing, China

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第5讲：实现CO_2捕集的煤粉富氧燃烧发电技术

(工程原理)

Stanley Santos

IEA Greenhouse Gas R&D Programme

亚太伙伴计划富氧燃烧能力建设课程

中国，北京

2010.3.15

Overview

- ***Introduction – Oxyfuel Combustion***
- ***Overview to the Boiler and Burner Development***
  - Recycle of Flue Gas
  - Emissions (NOx and SOx)
- ***Overview to the Oxygen Production***
  - 2 column design – “Oxyton Cycle”
  - Double reboiler design
- ***Overview to the CO2 Processing Unit***
  - NOx and SOx reaction during compression
  - Removal of Inerts
- ***Concluding Remarks***

概述

- *引言 – 富氧燃烧*
- *锅炉燃烧器的发展概述*
  - 烟气再循环
  - 污染物排放 (NOx、SOx)
- *制氧系统概述*
  - 双塔设计– “Oxyton Cycle”
  - 双蒸发器设计
- ***CO_2*处理单元概述**
  - 压缩期间有关NOx 、SOx 的反应
  - 脱除惰性气体
- *结束语*

Introduction

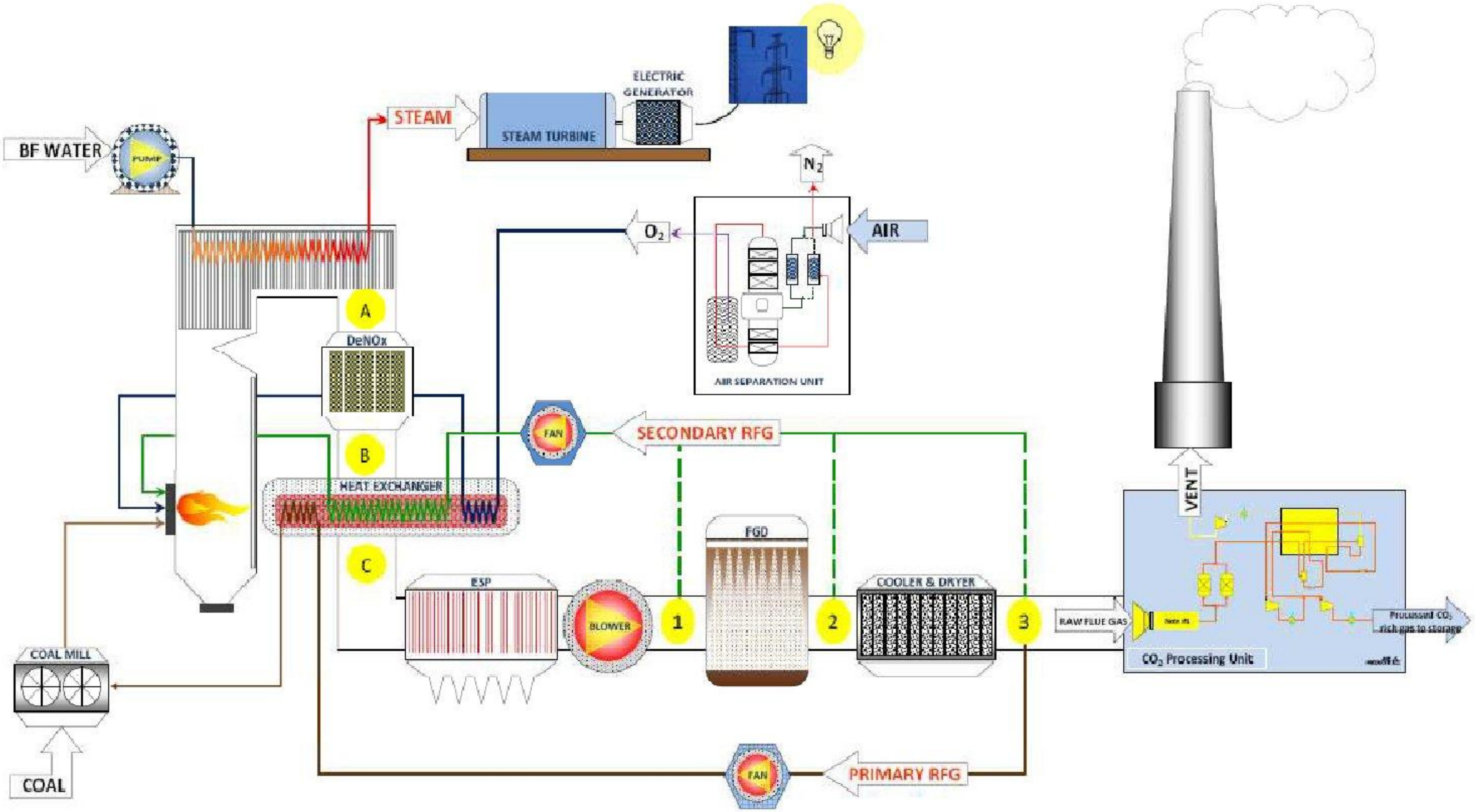
OXY-PULVERIZED COAL COMBUSTION FOR POWER GENERATION

引言

煤粉富氧燃烧发电

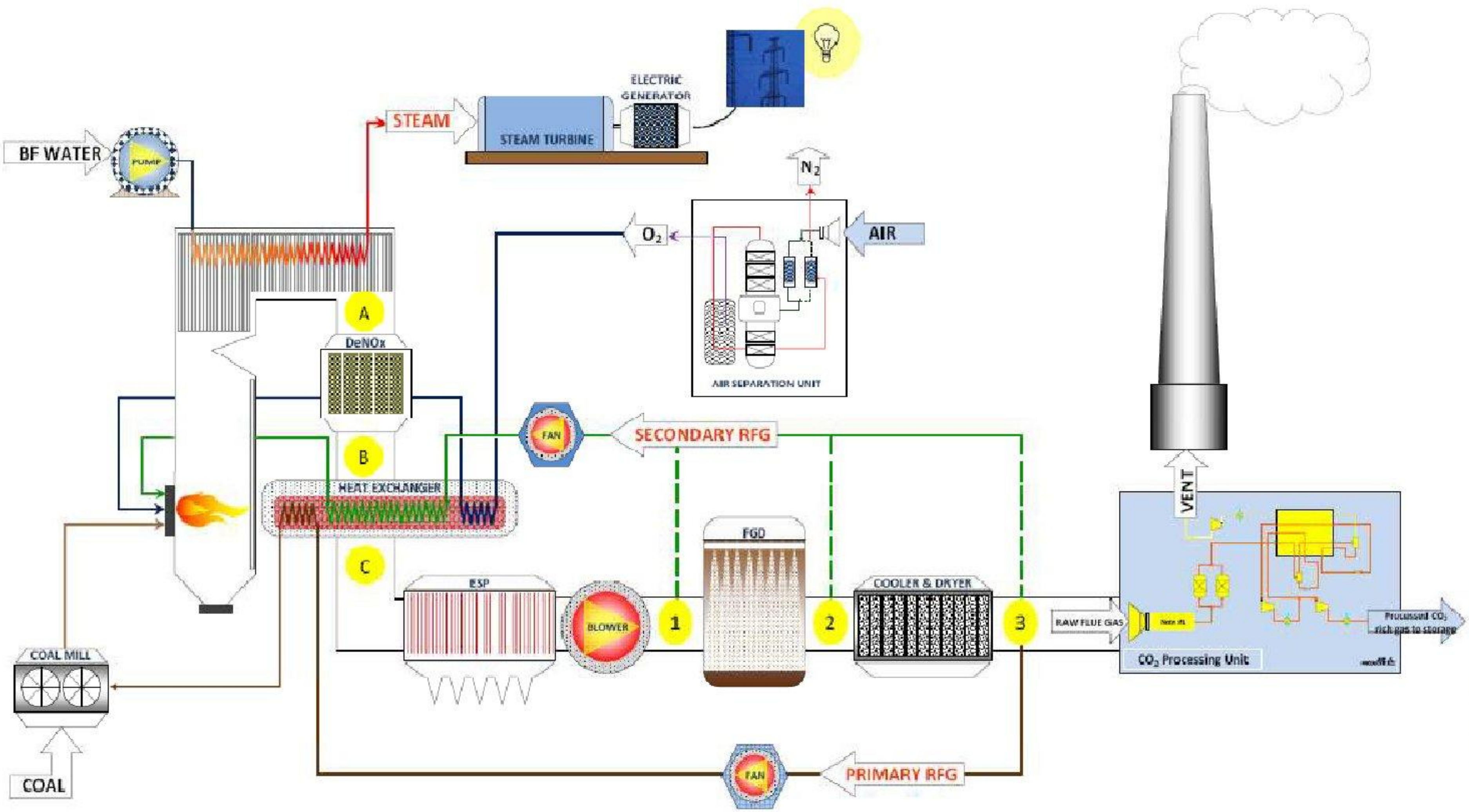
Introduction

Oxyfuel Combustion for Coal Fired Power Plant with CO_2 Capture



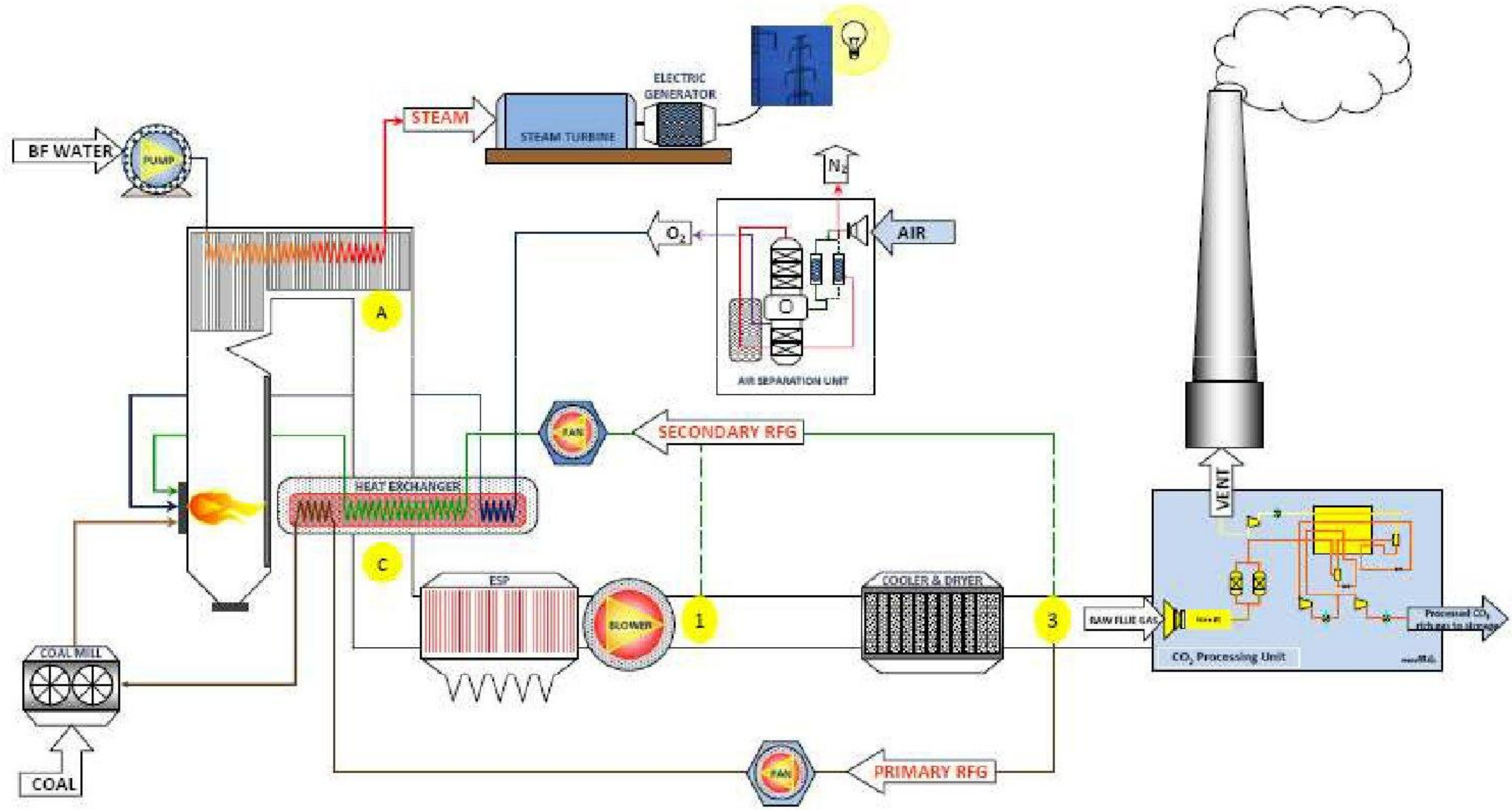
引言

有CO_2 捕集的煤粉富氧燃烧发电技术

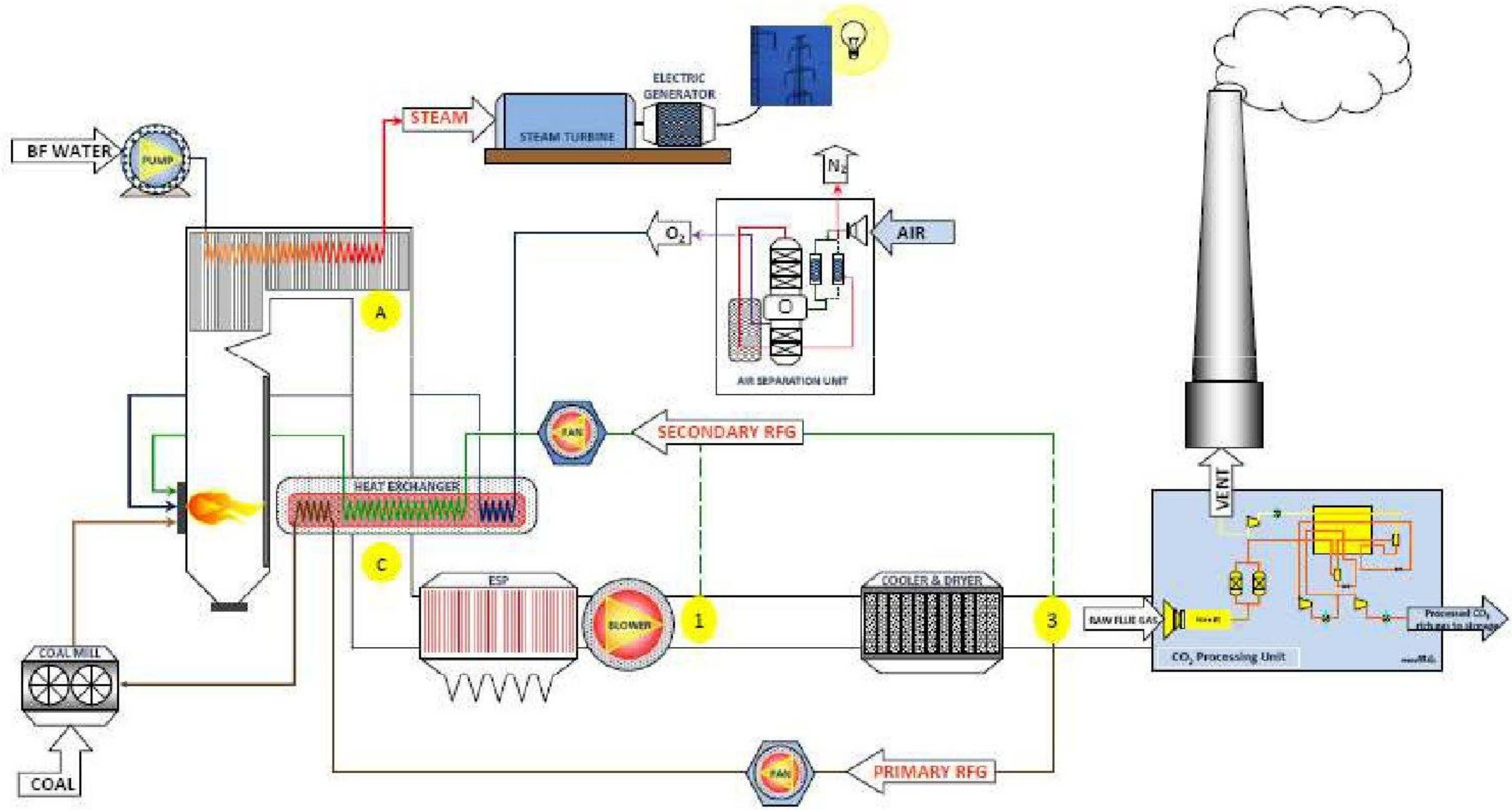


Where Can You Extract the Recycled Flue Gas (RFG)

(For some practical application using low S coal)



抽取再循环烟气（RFG）的位置
(针对低硫煤的实际运行)



Overview to Boiler and Burner Development

IMPACT OF RECYCLE FLUE GAS TO THE BOILER OPERATION

锅炉、燃烧器发展概述

再循环烟气对锅炉运行的影响

Factors affecting Recycle Ratio

- ***Critical factors affecting the optimum amount of recycled flue gas***
  - Burner and boiler design (heat transfer and flame stability – oxygen distribution through burner)
  - Air ingress
  - Purity of oxygen from the ASU
  - Coal type
  - Level of moisture content in comburent
  - Comburent (oxidant) temperature

再循环率的影响因素

- ***最佳再循环烟气量的关键影响因素***
  - 燃烧器和锅炉设计
    (传热、火焰稳定性——燃烧器的O_2分布)
  - 漏风
  - 来自ASU的O_2纯度
  - 煤种
  - 助燃气体的水分含量
  - 助燃气体（氧化剂）温度

Mass balance calculation should have a firm basis!!!

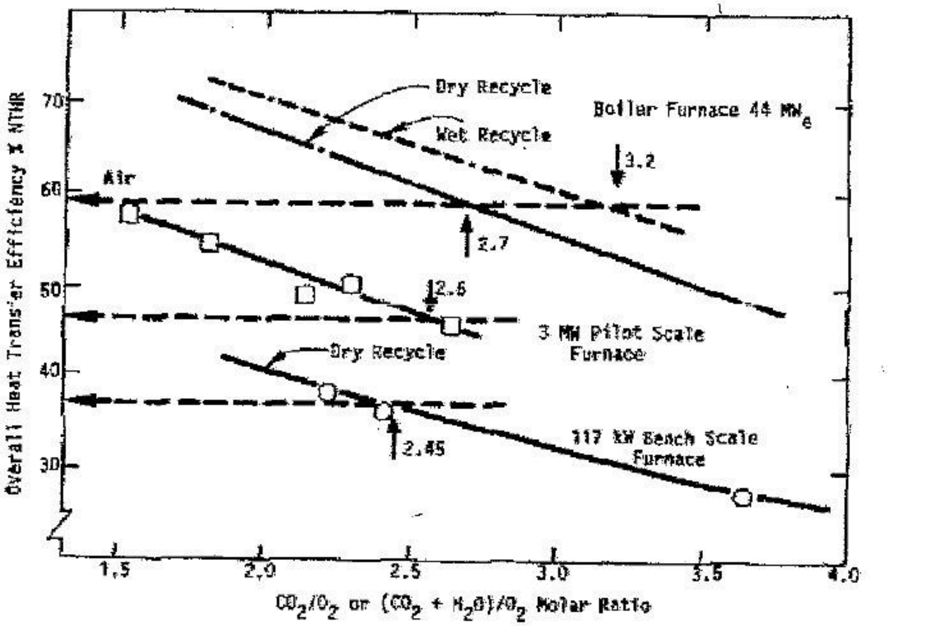
Primary control of the boiler is in the oxygen content of the flue gas (~3.5%vd)

Requirements of the coal mill should define the quality of the primary RFG

- Defining how the burners should operate is a required step… We need to establish criteria that would result to good combustion. An important element to your process control.

Criteria for heat transfer profile should define the quality of secondary RFG

- Molar ratio of the oxidant
- O_2 concentration in the secondary comburent



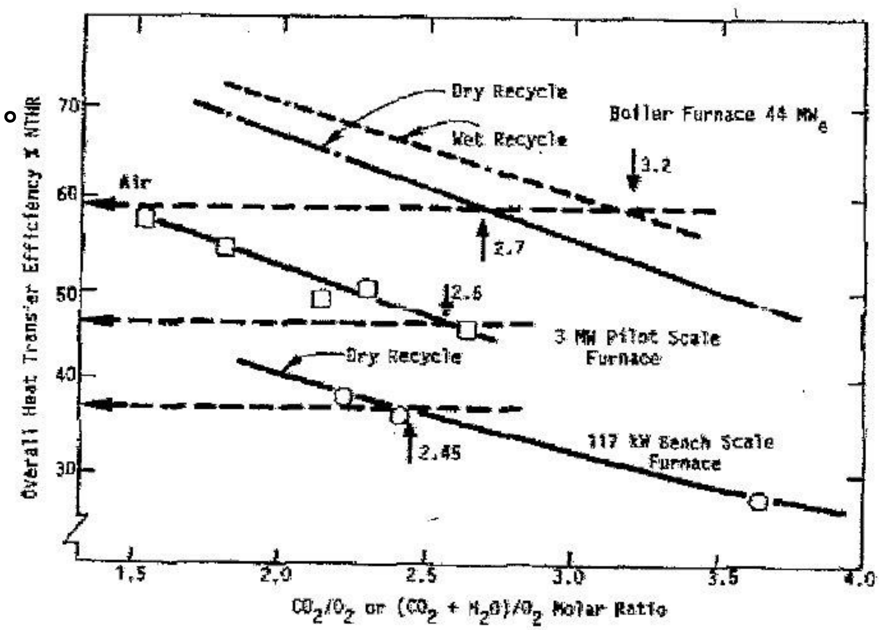
Data from ANL studies (1989)

质量平衡计算作为坚实的基础

锅炉运行主要的控制是烟气中的氧含量(~3.5%vd)

磨煤机的要求决定了一次再循环烟气的特性。

确定燃烧器如何运行是必要步骤。
我们需要设立保证燃烧效果的标准。
这是过程控制的重要因素。



传热分布将确定二次再循环烟气的特性

Data from ANL studies (1989)

- 氧化剂的摩尔比
- 二次助燃风中的O_2浓度

Optimum Recycle Ratio

Table 1: Some of the reported results for the optimum flue gas recycle ratio

	Burner Rating	Type of flue gas	Molar ratio[1] $(CO_2 + H_2O)/O_2$	% O_2 in Comburent[2]	Recycle Ratio[3] RFG / (RFG + PFG)
ANL (EERC)	3 MW_{th}	dry recycle	2.66	~29%	-
		wet recycle	3.25	~31%	~0.68
IFRF	2.5MW_{th}	wet recycle	~2.20	~48%	0.58
IHI	1.2MW_{th}	wet recycle	-	32% - 36%	-
CANMET	300 kW_{th}	wet recycle	-	35%	-

[1] Molar ratio of the comburent (oxidant)
[2] %oxygen through the burner throat
[3] RFG and PFG are the mass flow rate of the recycle flue gas and the product flue gas respectively

最佳循环率

表1　烟气最佳循环率的结果

	燃烧器等级	再循环烟气种类	摩尔比[1] $(CO_2 + H_2O)/O_2$	助燃气体中[2] O2（%）	循环比[3] RFG / (RFG + PFG)
ANL (EERC)	3 MW_{th}	干循环	2.66	~29%	-
		湿循环	3.25	~31%	~0.68
IFRF	2.5MW_{th}	湿循环	~2.20	~48%	0.58
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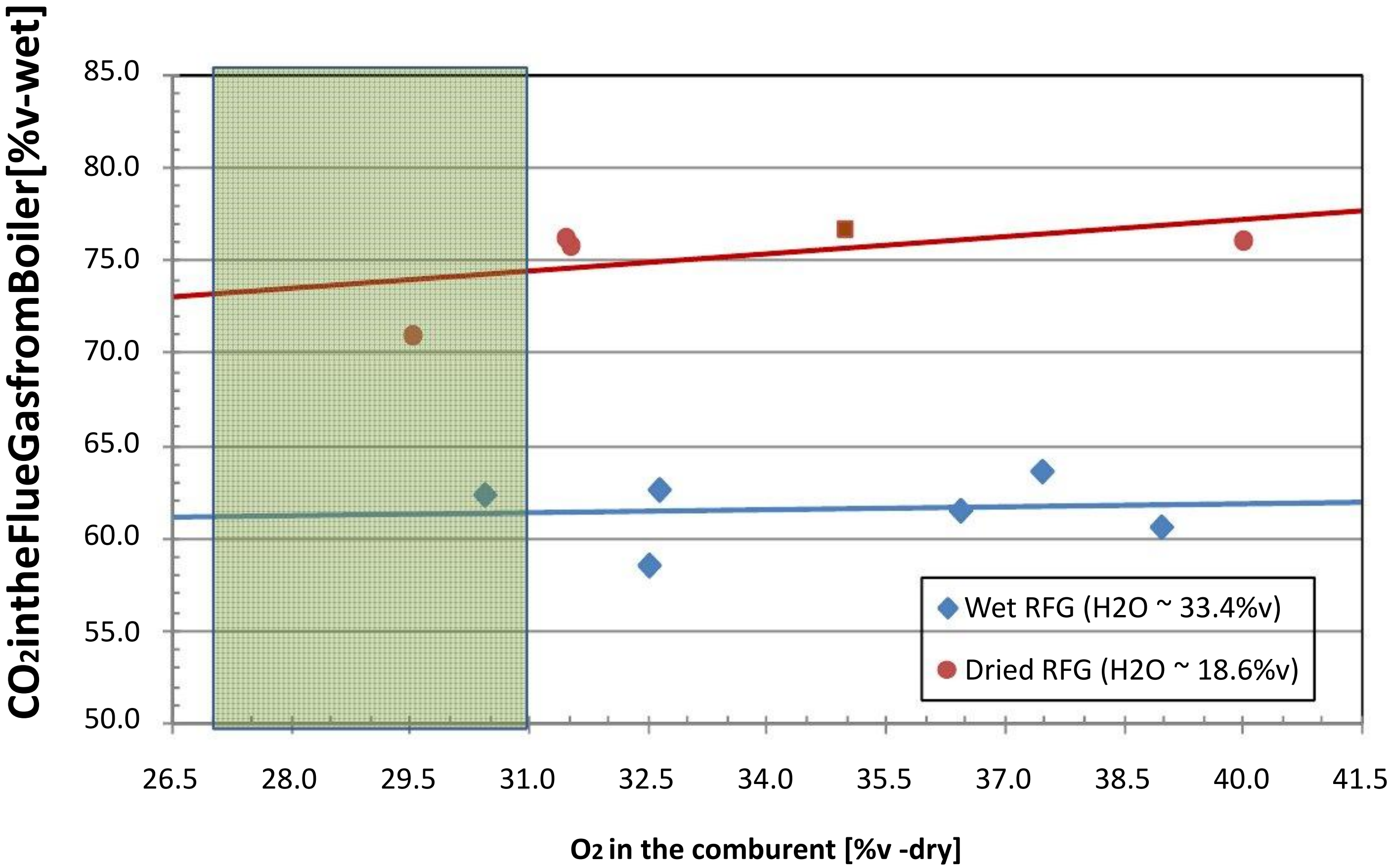
CANMET	300 kW_{th}	湿循环	-	35%	-

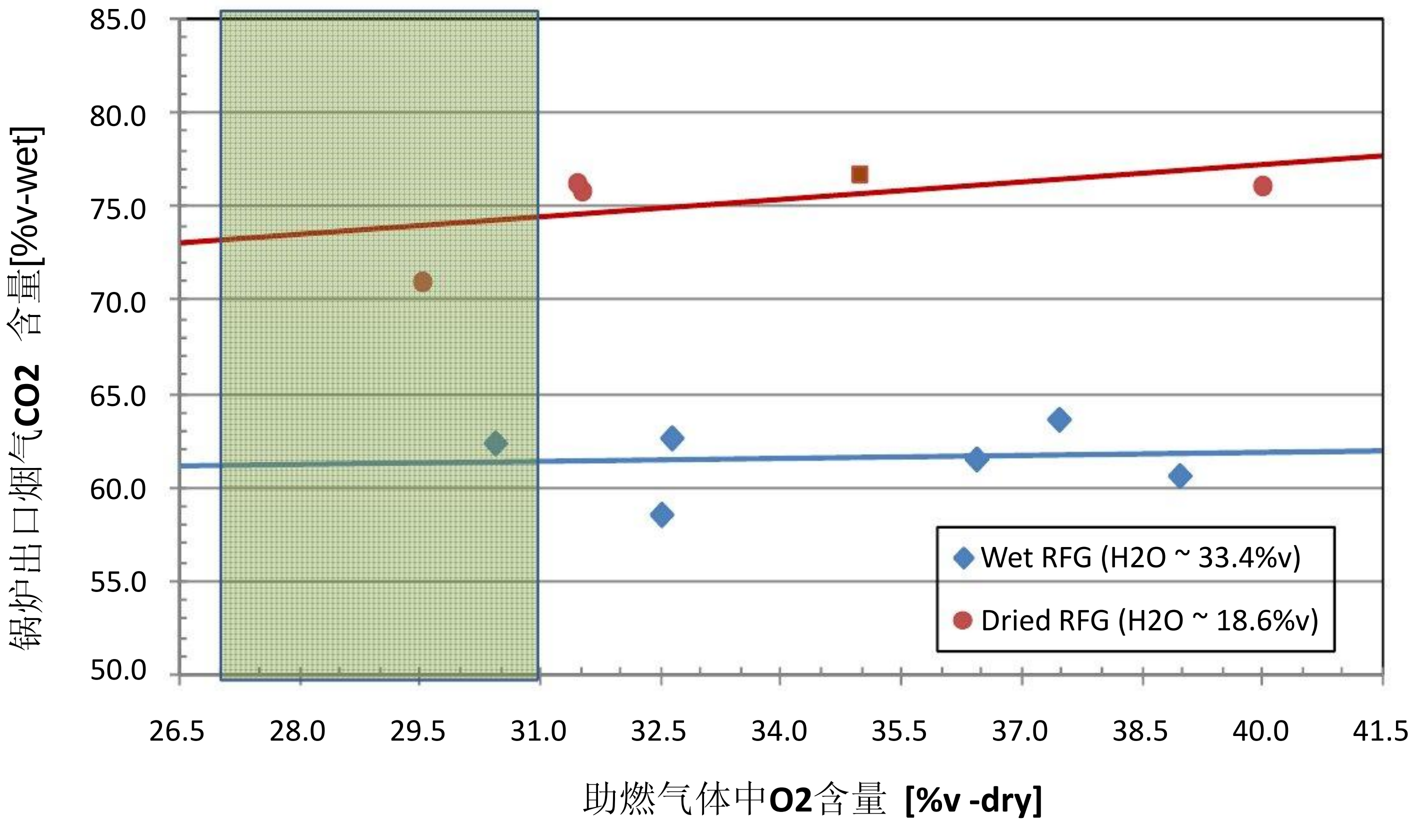
[1]氧化剂的摩尔比
[2]燃烧器喉部的氧浓度
[3]RFG和PFG分别是再循环烟气和出口烟气的质量流率

Impact of the moisture content of the Recycled Flue Gas



Data from ANL studies (1987)

再循环烟气中水分含量的影响



Data from ANL studies (1987)

Flame Description – Impact of Recycle Ratio
(Courtesy of IFRF)

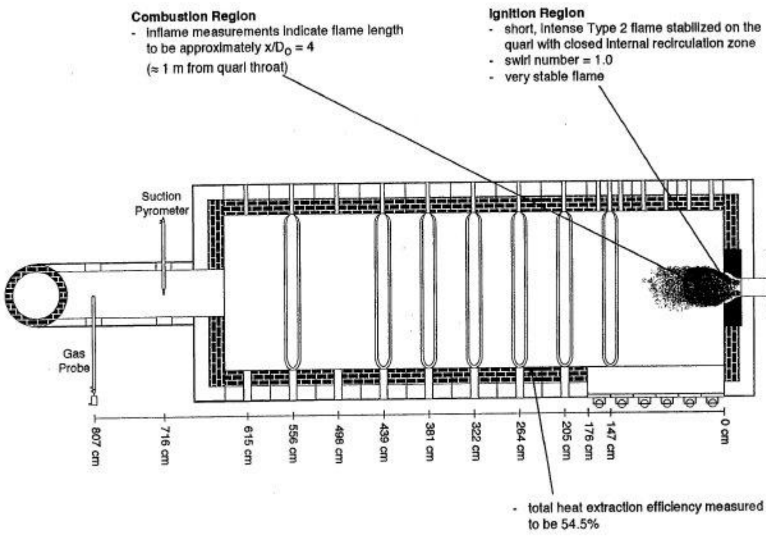


Figure 3(a): normal air-fired operation

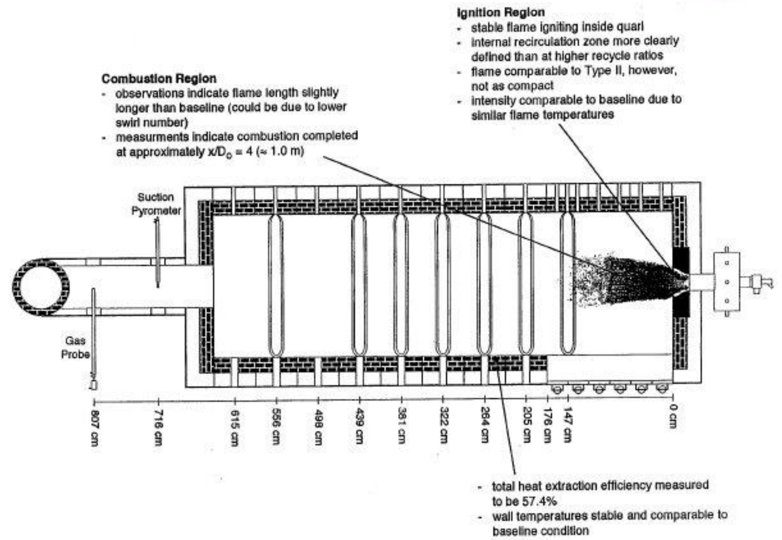


Figure 3(b): O2-RFG flame with recycle ratio = 0.58

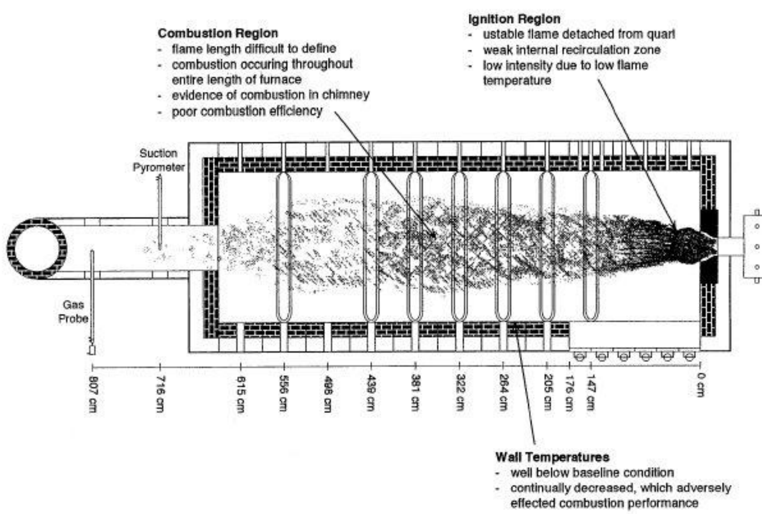


Figure 3(c): O2-RFG flame with recycle ratio = 0.76

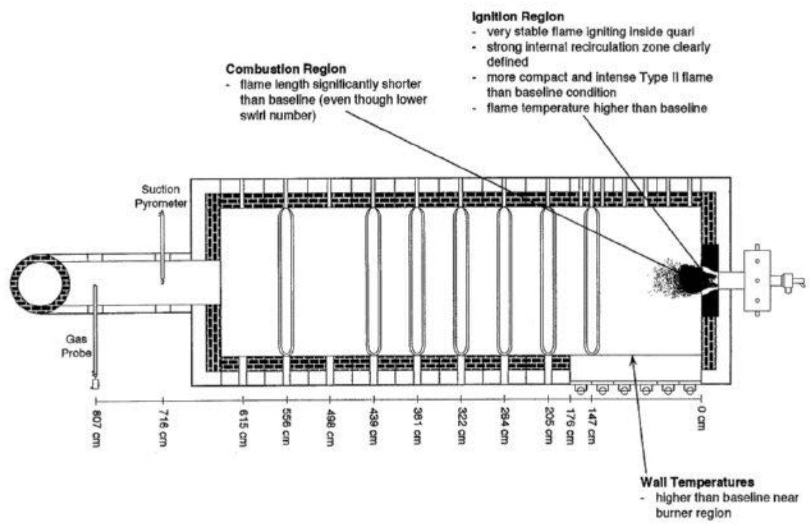


Figure 3(d): O2-RFG flame with recycle ratio = 0.52

火焰特性——循环比的影响

(Courtesy of IFRF)

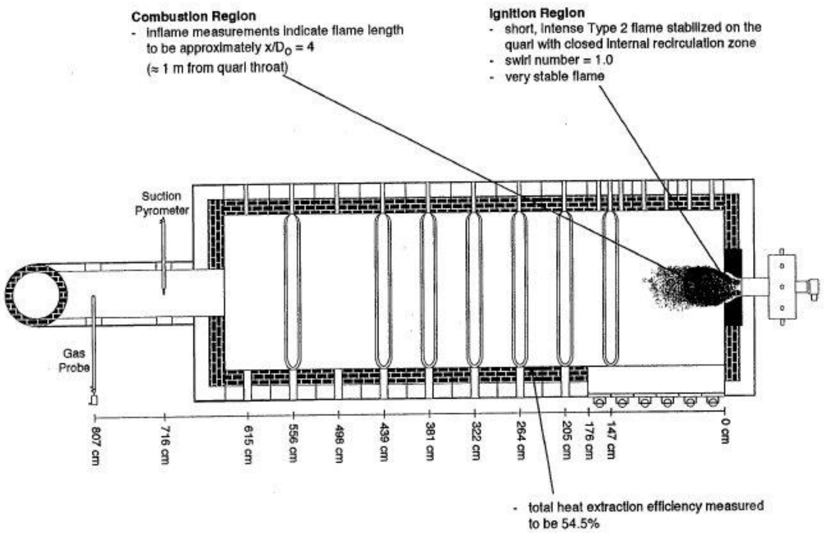


图3（a）常规空气燃烧

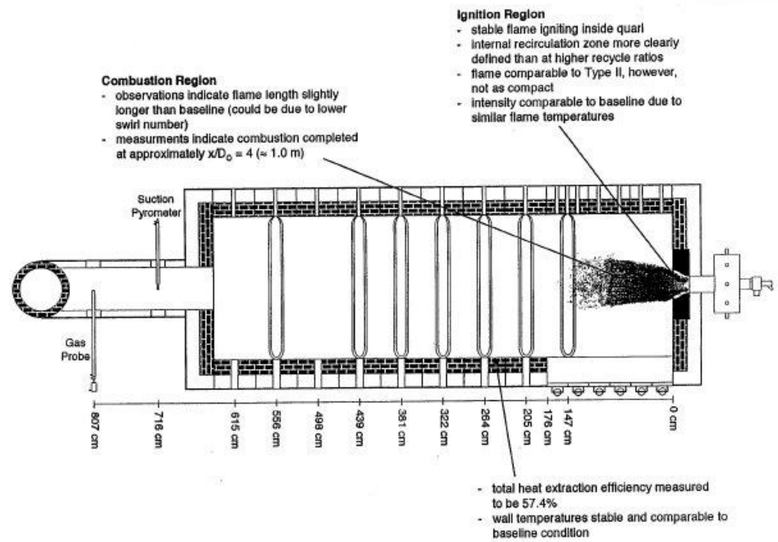


图3（b）：循环比= 0.58时 O2-RFG 火焰

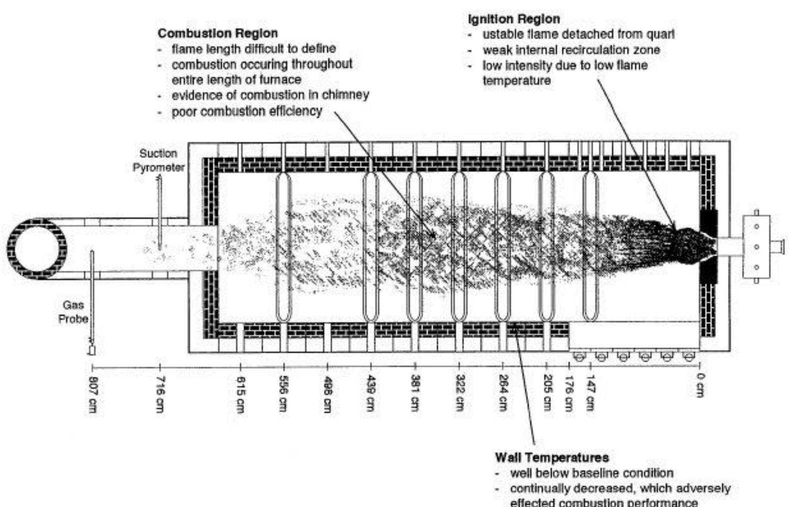


图3(c): 循环比=0.76时O2-RFG 火焰

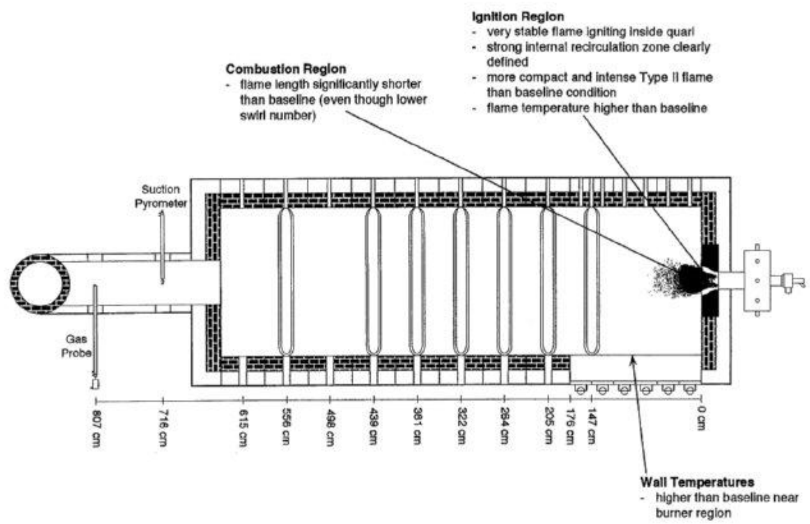
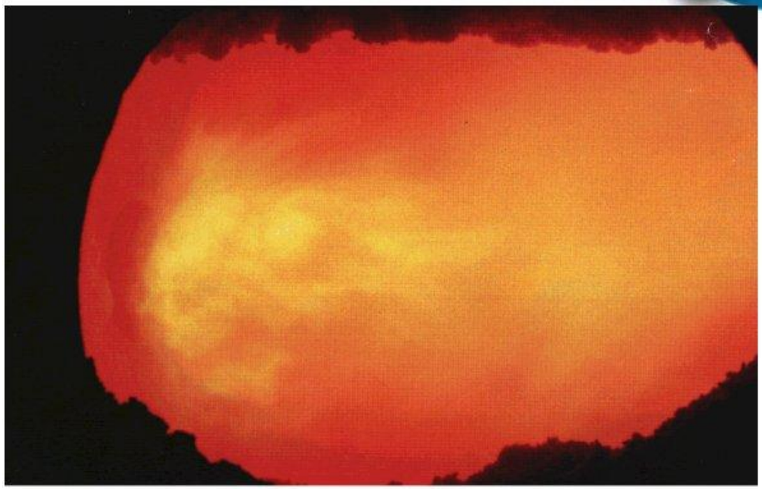
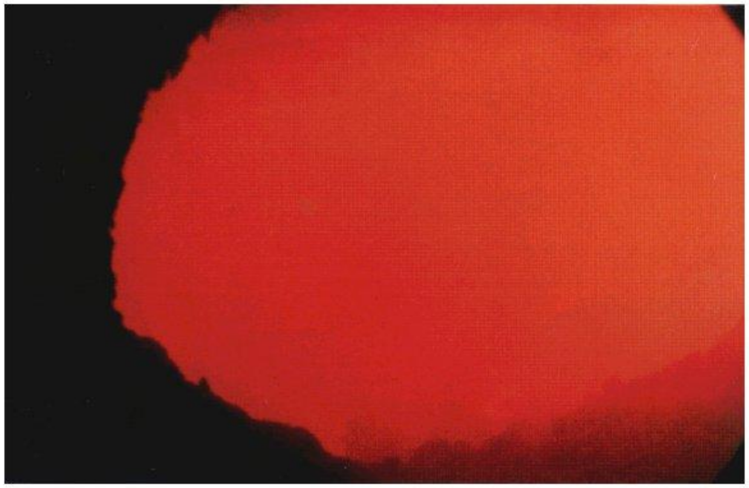


图 3(d): 循环比= 0.52时O2-RFG火焰

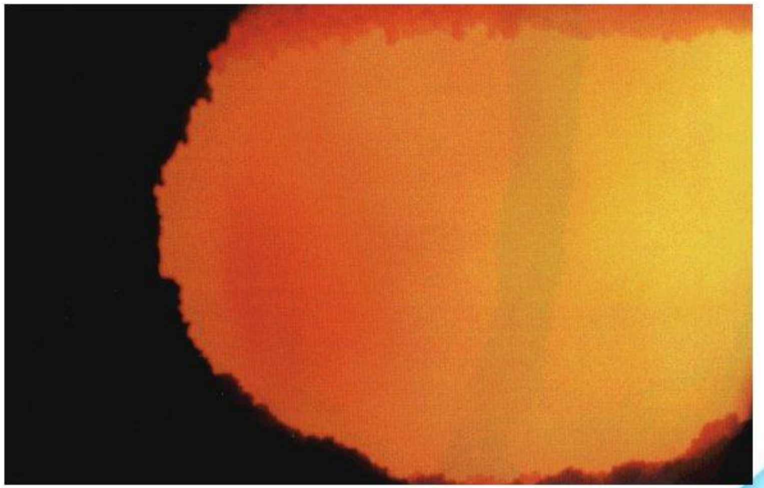
Coal Flame Photos: Air Fired vs Oxy-Fired (Courtesy of IHI)



Air mode（O_2：21%）

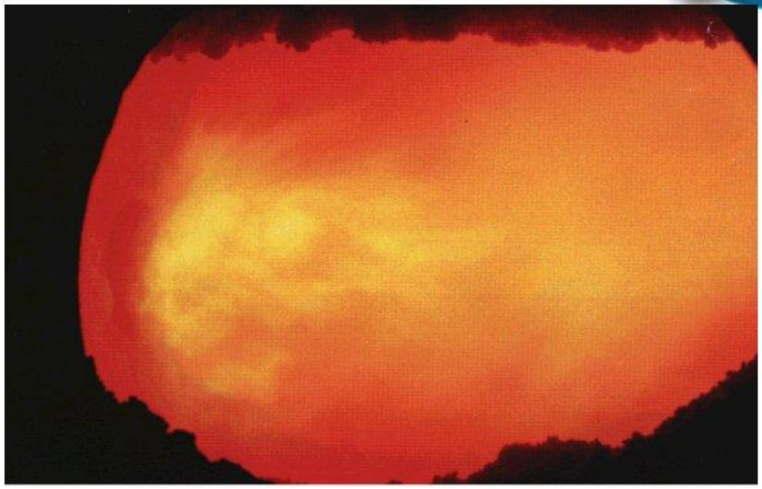


Oxy mode（O_2：21%）

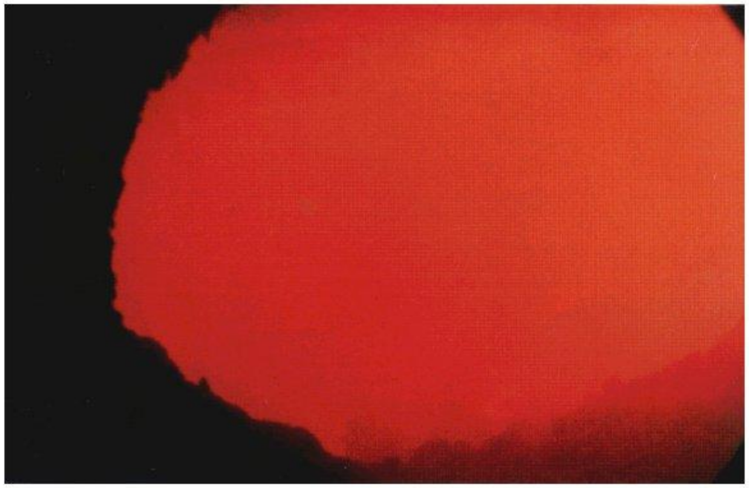


Oxy mode（O_2：30%）

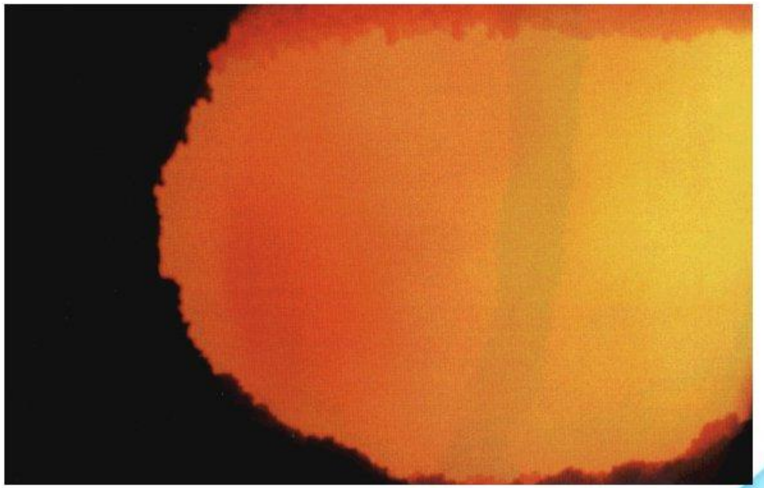
煤燃烧火焰图:
空燃vs 富氧燃烧
(Courtesy of IHI)



空燃模式（O2：21%）



富氧模式（O2：21%）



富氧模式（O2：30%）

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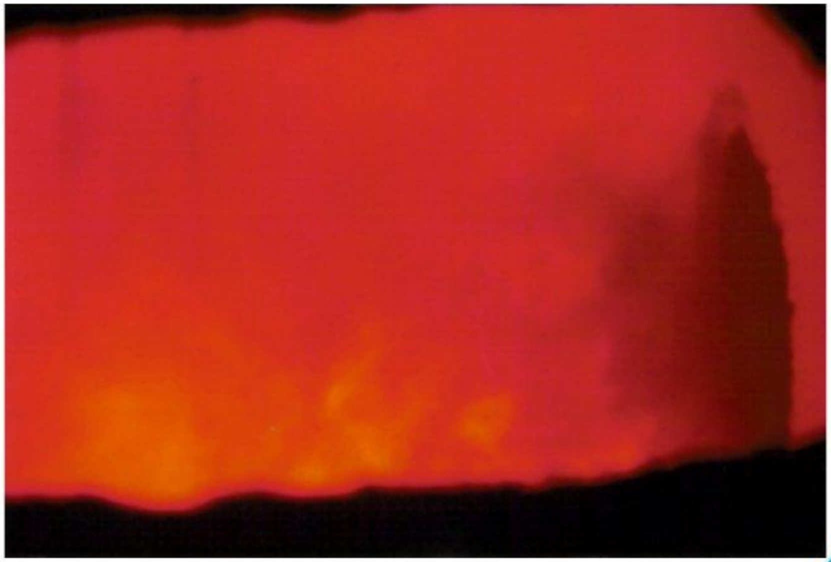
Coal Flame Photos: Impact of Recycled Flue Gas (Courtesy of IFRF)

Recycle Ratio = 0.58
(~ 0.61 include the CO_2 to transport coal)



Recycle Ratio = 0.76

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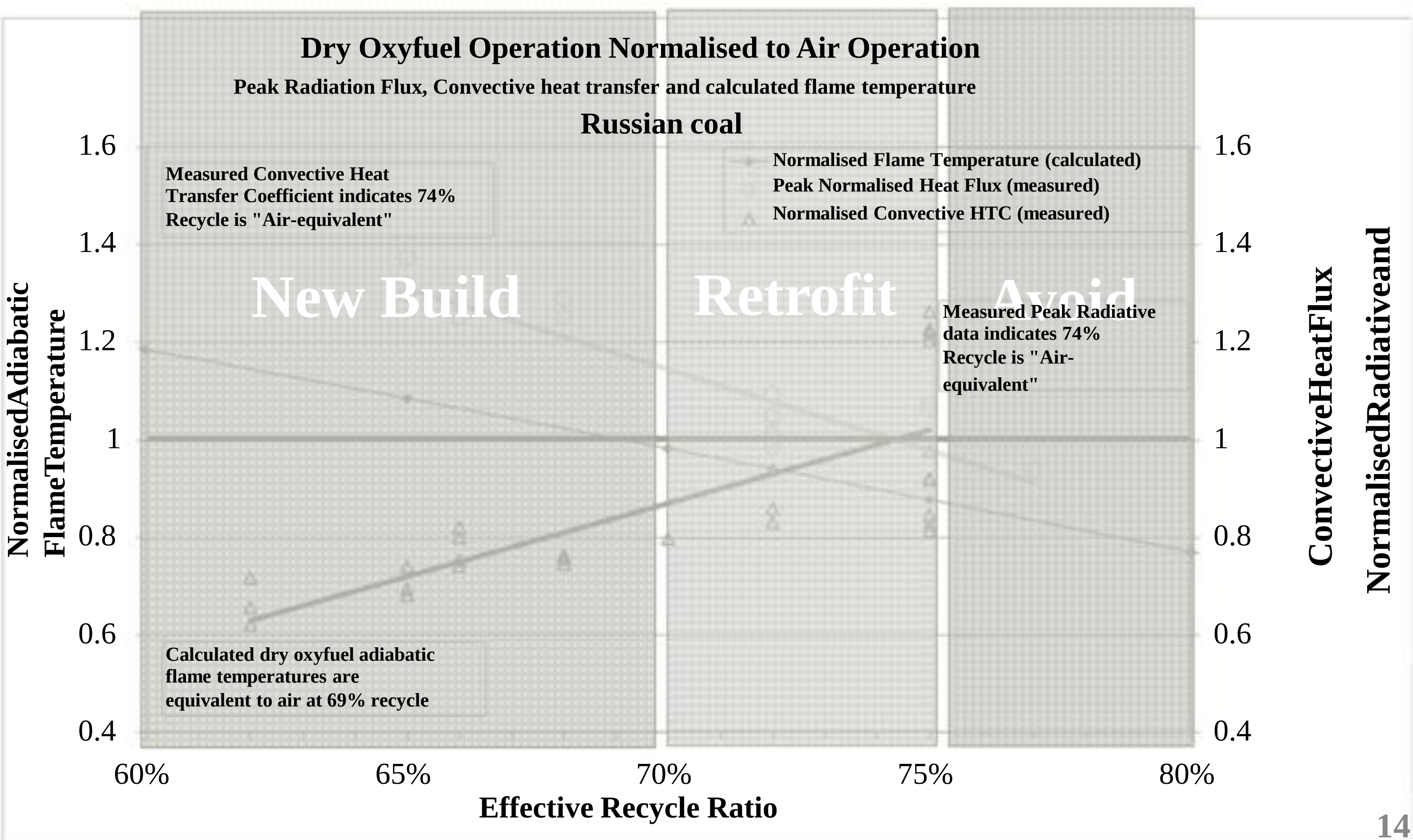
煤燃烧火焰图:
再循环烟气的影响
(Courtesy of IFRF)

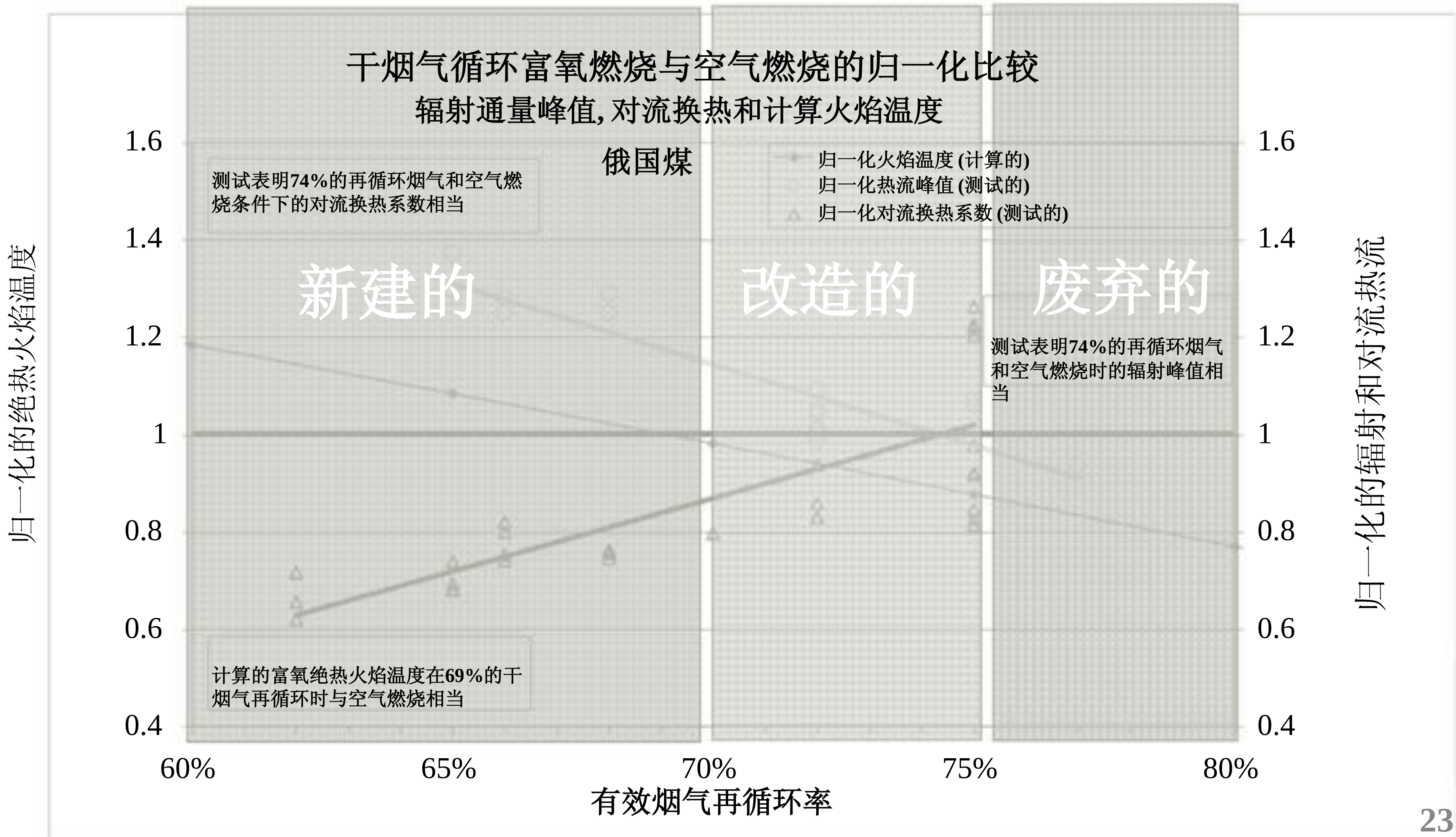
Recycle Ratio = 0.58
(~ 0.61 include the CO_2 to transport coal)

Recycle Ratio = 0.76

Normalised Convective & Radiative heat flux – Russian Coal - Dry Recycle



归一化对流、辐射热通量
– 俄国煤 – 干烟气循环



Considerations in the Boiler Operation

O_2 Purity and Air Ingress

(a.) Why not 99+% O_2 Purity
(b.) Air Ingress… A Challenge for the Operator

锅炉运行方面的因素

O_2 纯度和漏风

(a.) 为何不是 99+% O_2 纯度

(b.) 漏风……运行的挑战

Issue of Air Ingress (Air In-leakage)

Air Ingress in the boiler is a fact of life!!!

1st Large Scale Demonstration of Oxy-Coal Combustion (35MWth) – What Are the Lesson Learned...

漏风问题 (漏入空气)

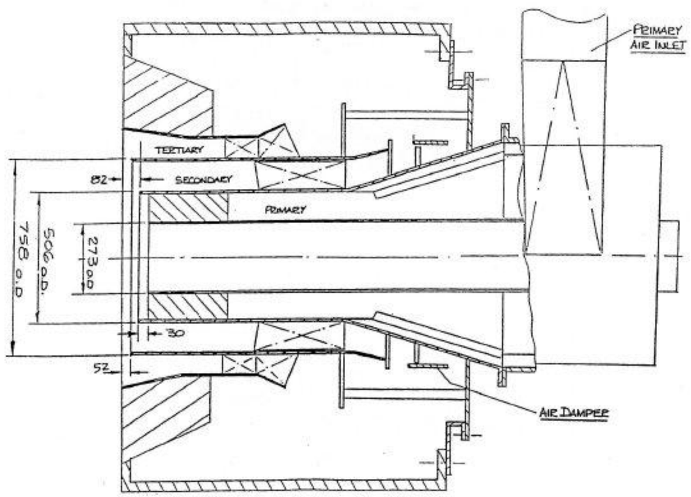
锅炉漏风是一个现实的问题!!!

首个大规模富氧燃烧示范电站 (35MWth)
—— 有哪些经验……

Problem with Air Ingress

1st Large Scale Oxy-Coal Combustion

Burner Test Experience - International Combustion Ltd.

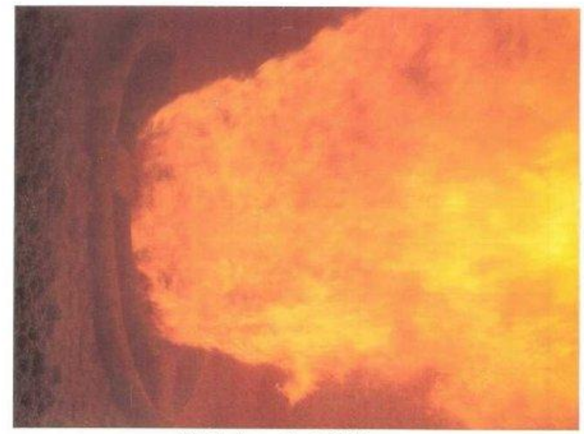


30 MWth Low NOx burner

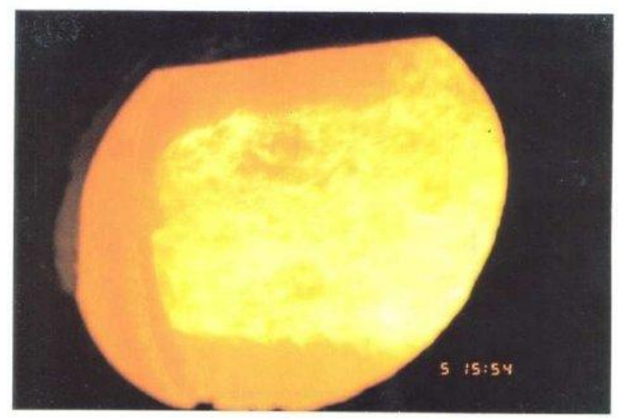
Because of Air Ingress the desired CO_2 composition (only ~ 28% dry basis).

Air Ingress in boilers

- approx. 3 % of flue gas flow for a new conventional power plant
- up to 10 % over the years for power plants in use



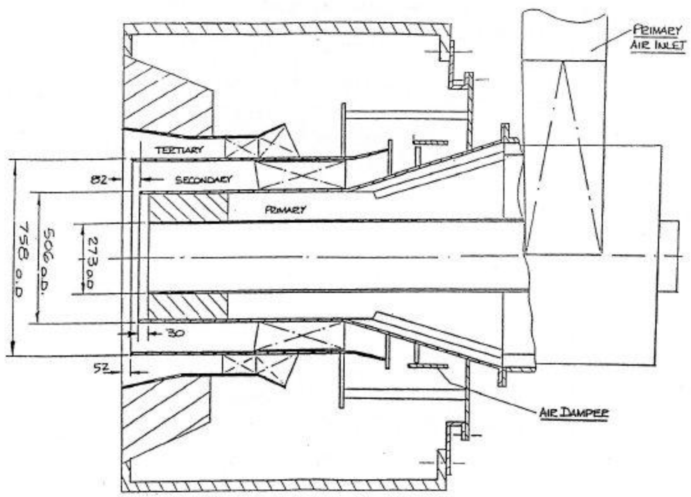
Test 1 - Conventional Air firing

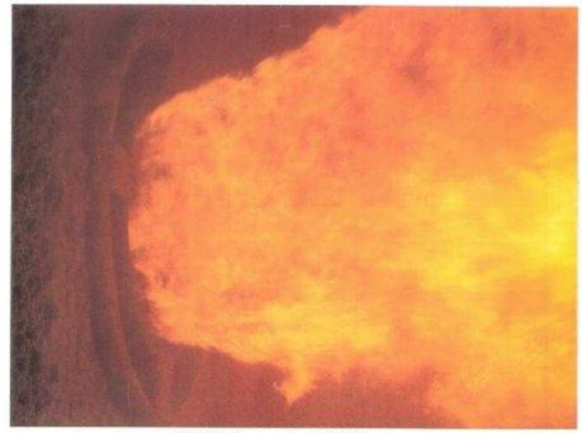


Test 3 - O_2/RFG Firing

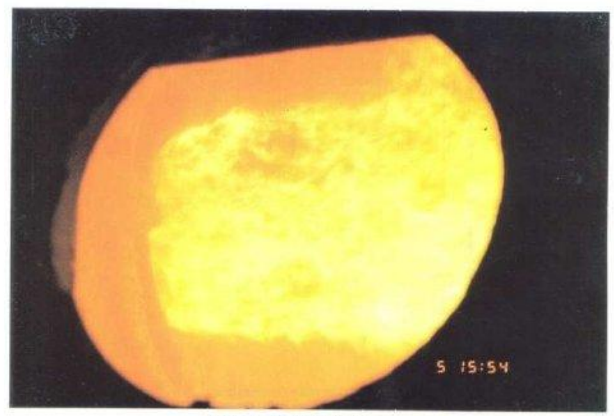
漏风问题

第一个大型富氧燃煤燃烧器测试
- 国际燃烧公司





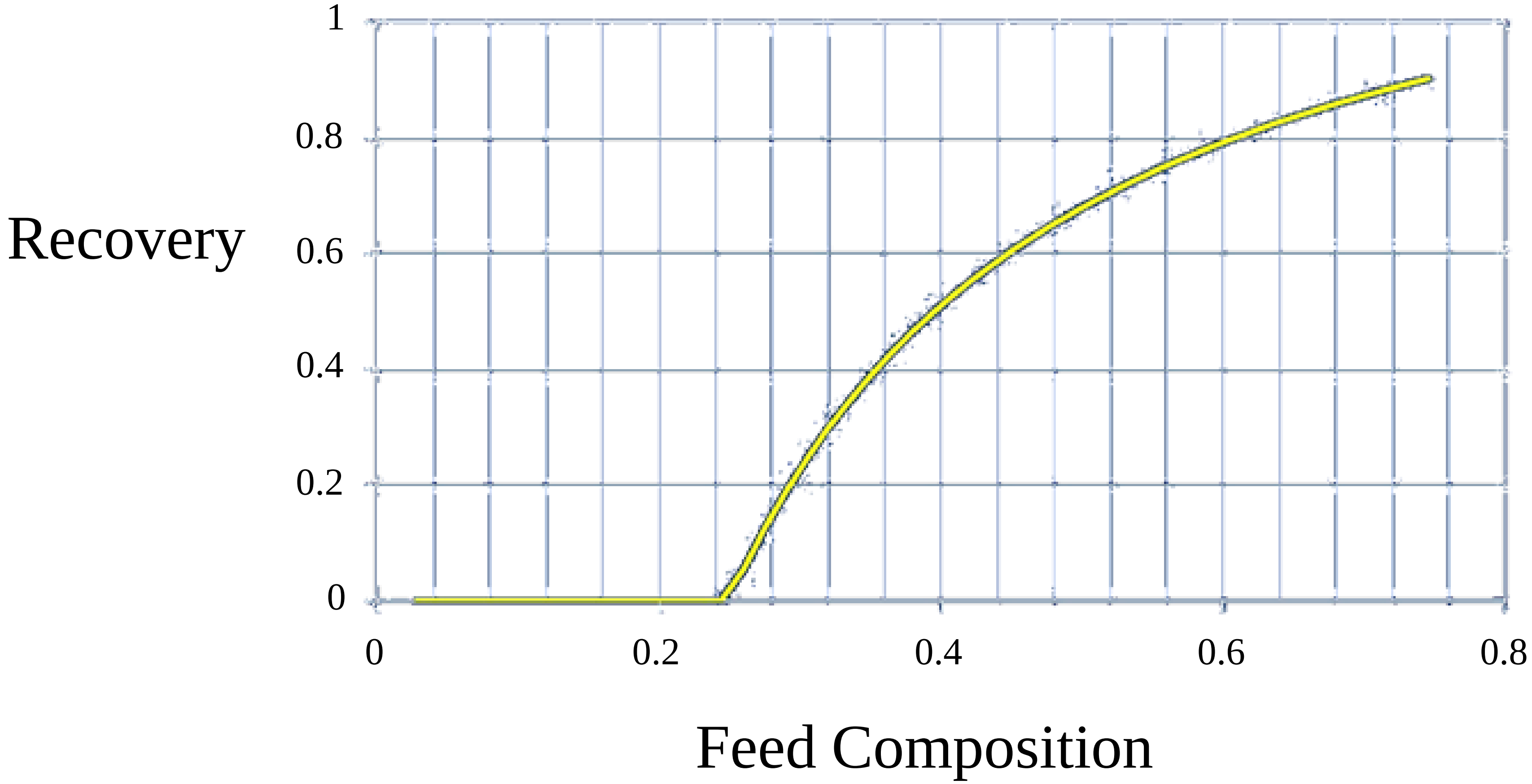
Test 1 - Conventional Air firing



Test 3 - O_2/RFG Firing

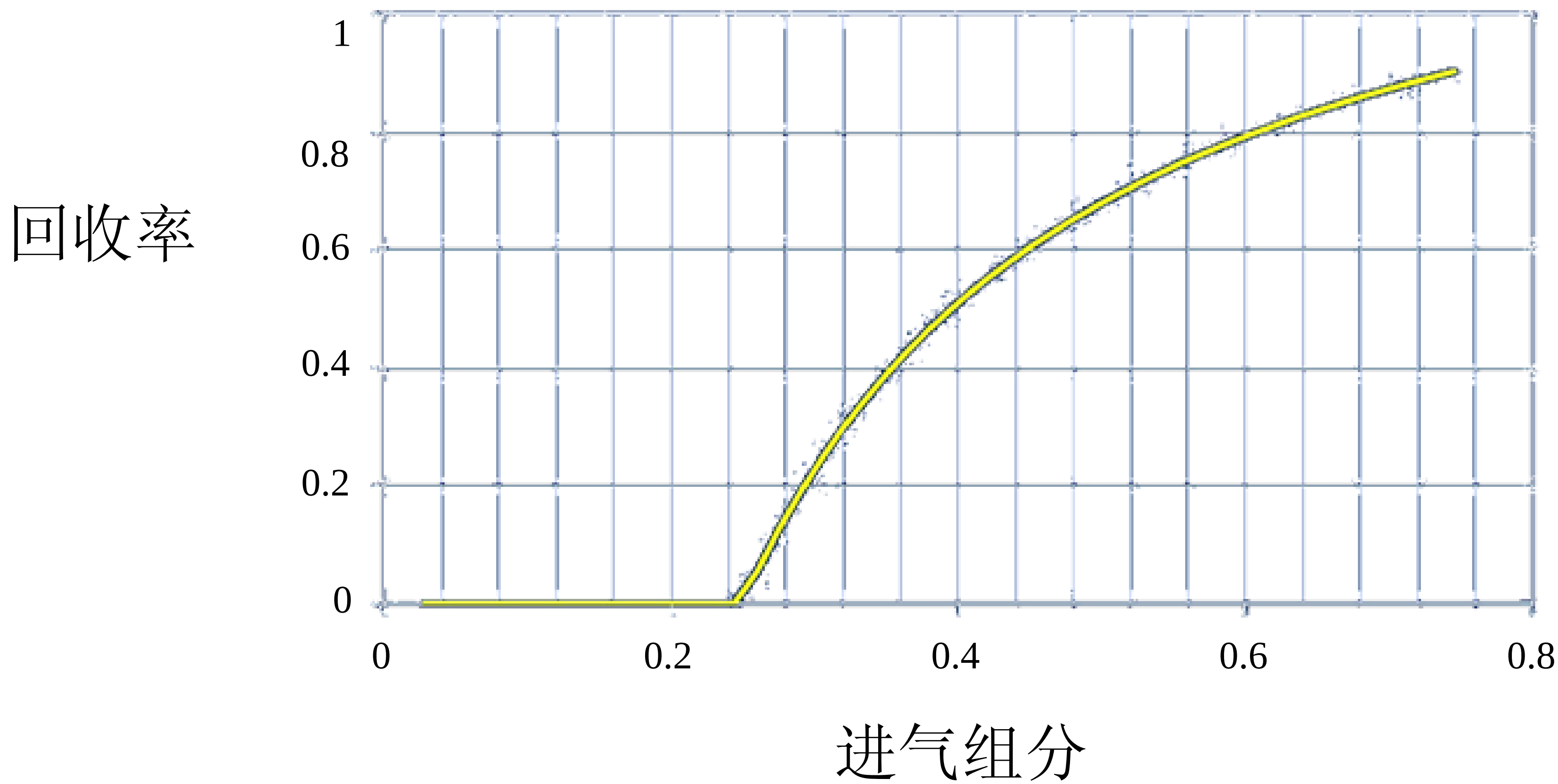
- ✓ 30 MWth 低 NOx 燃烧器
- ✓ 由于漏风，预期的CO_2含量(只有 ~ 28% ，干燥基)
- ✓ 锅炉中的漏风
  - ✓ 新建传统电站大约 3 % 烟气量的漏风量
  - ✓ 对已运行多年的电厂高达10 %烟气量的漏风量

CO_2 Recovery Depends On Feed Composition



At -55° C, 30 bar

CO_2回收率取决于进气组分



温度-55℃，压力- 30 bar

NOx Emissions

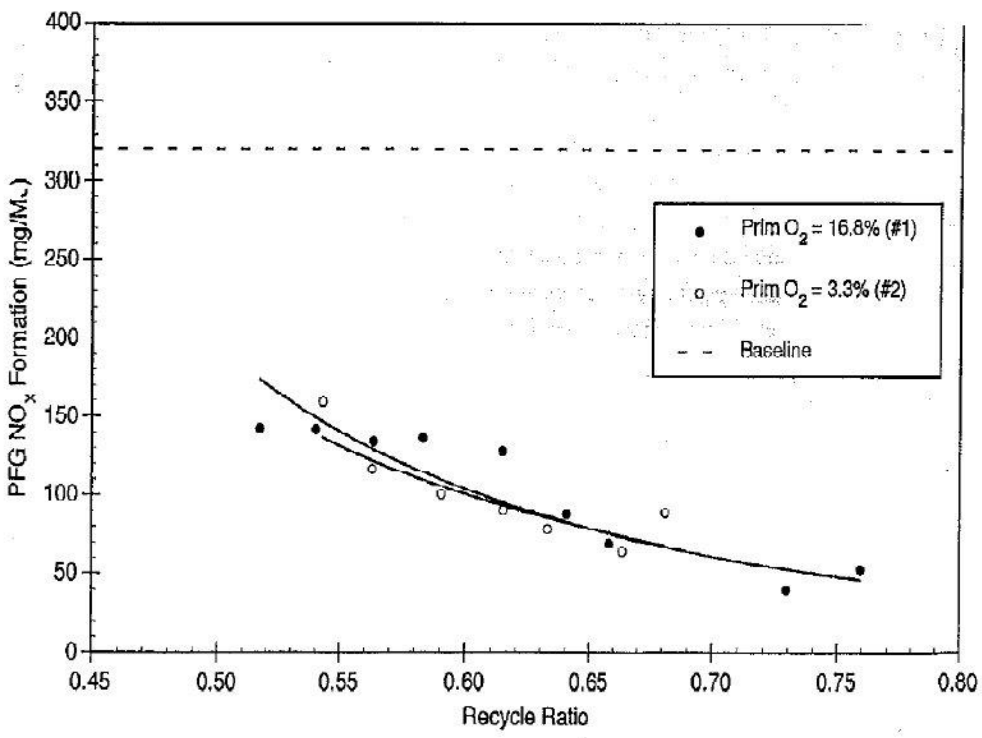
- We have quite a good confidence in knowing the trend of these emissions

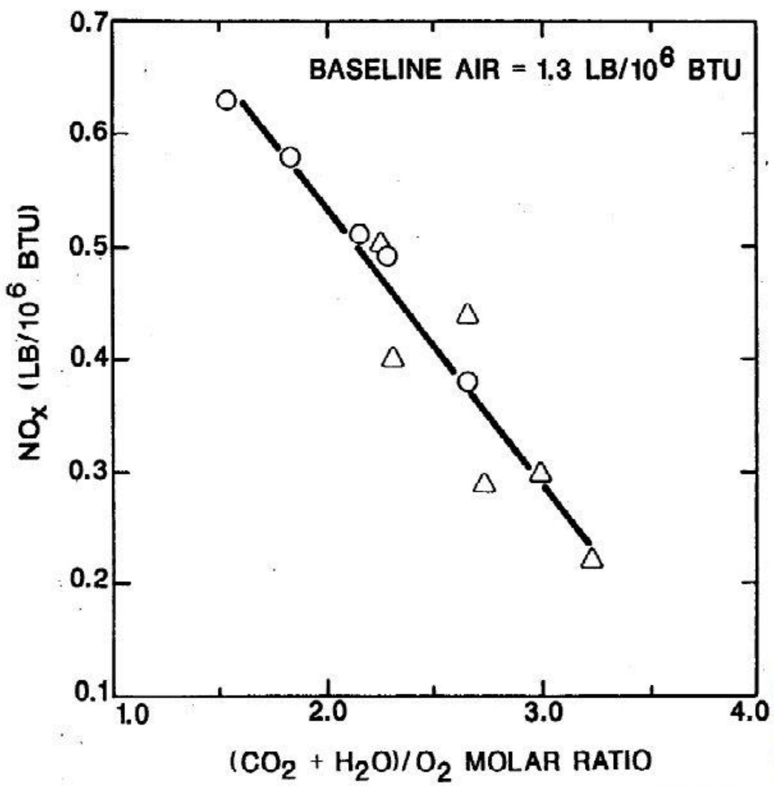
NOx 排放

——我们对排放趋势有相当高的信心

NOx Emissions

(Results from ANL-EERC and IFRF)





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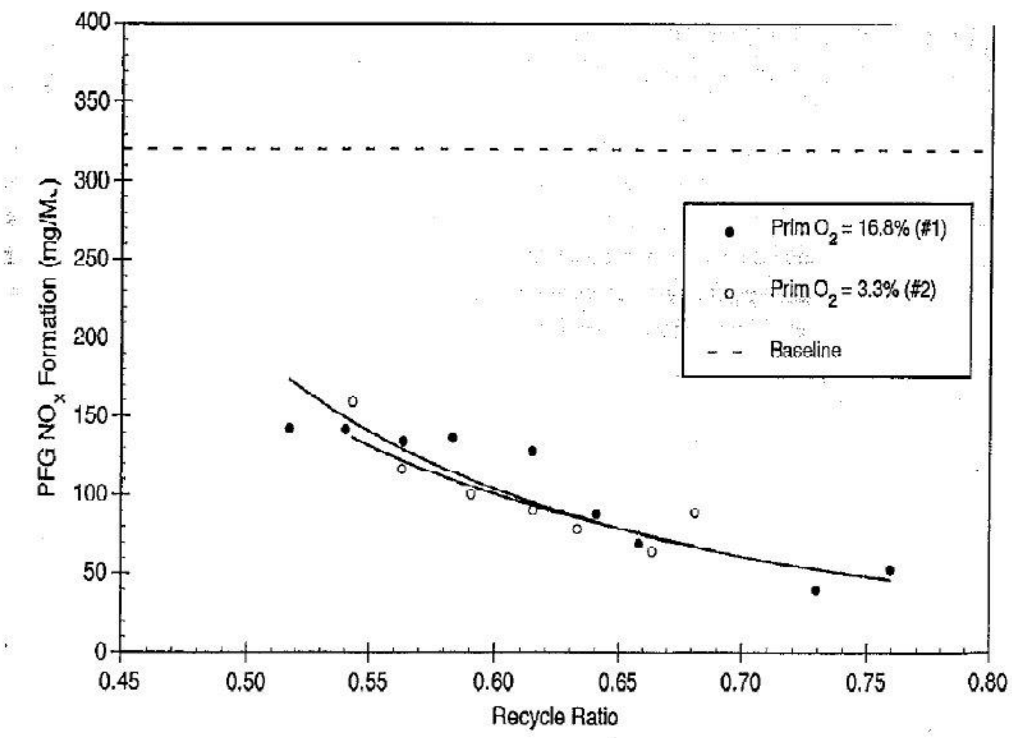
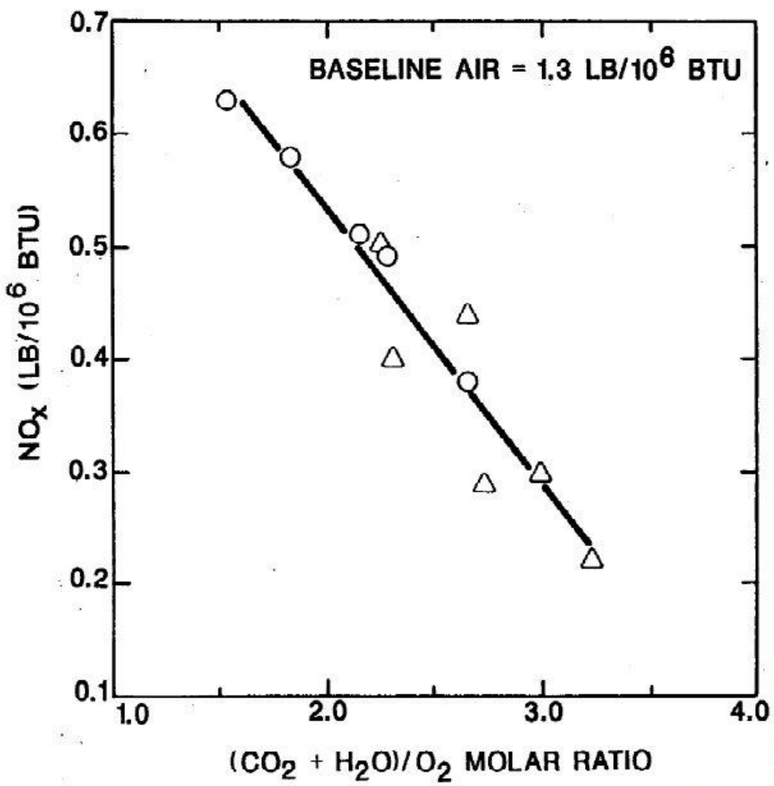
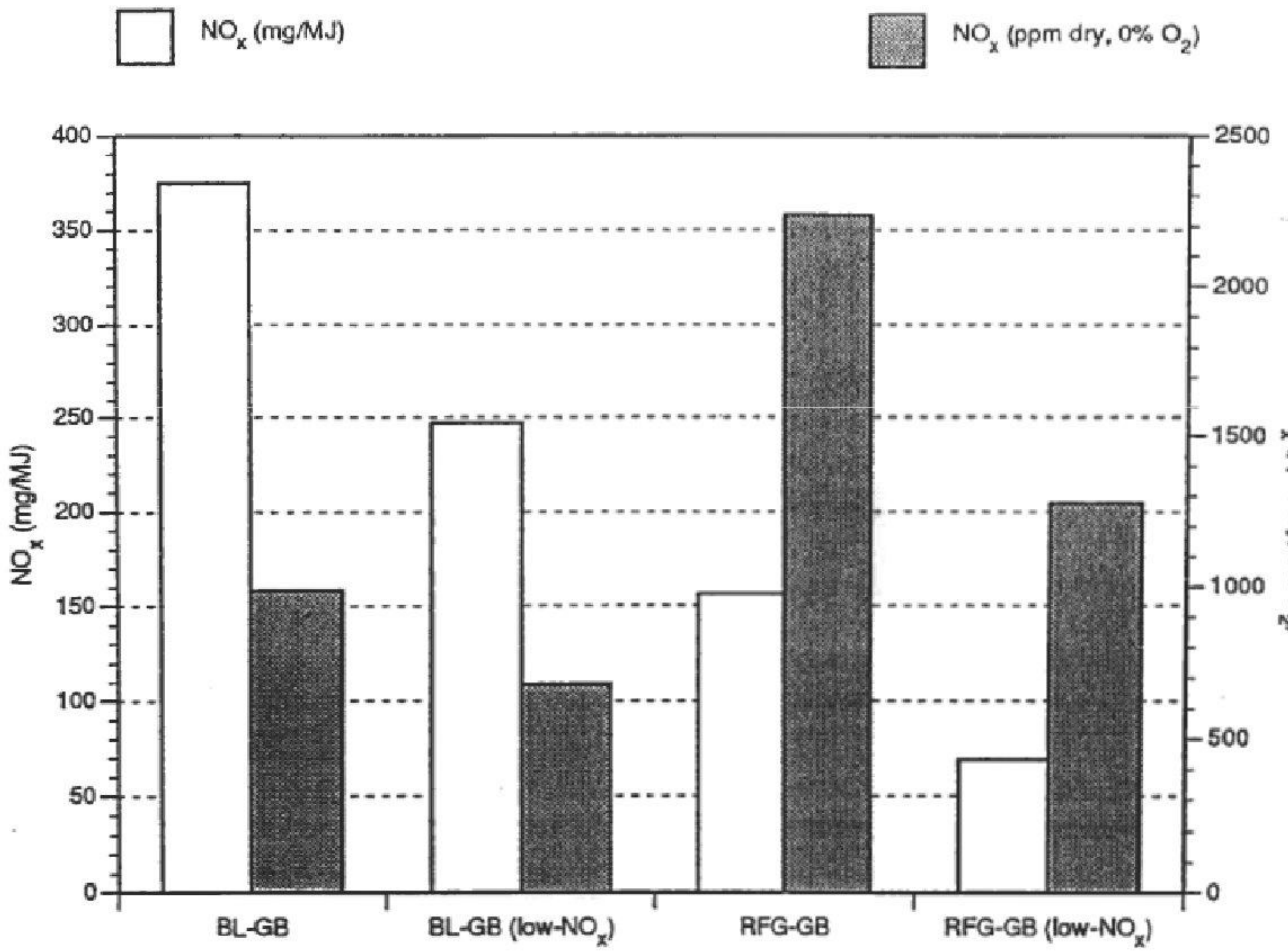
NOx 排放
(结果来自 ANL-EERC和IFRF)

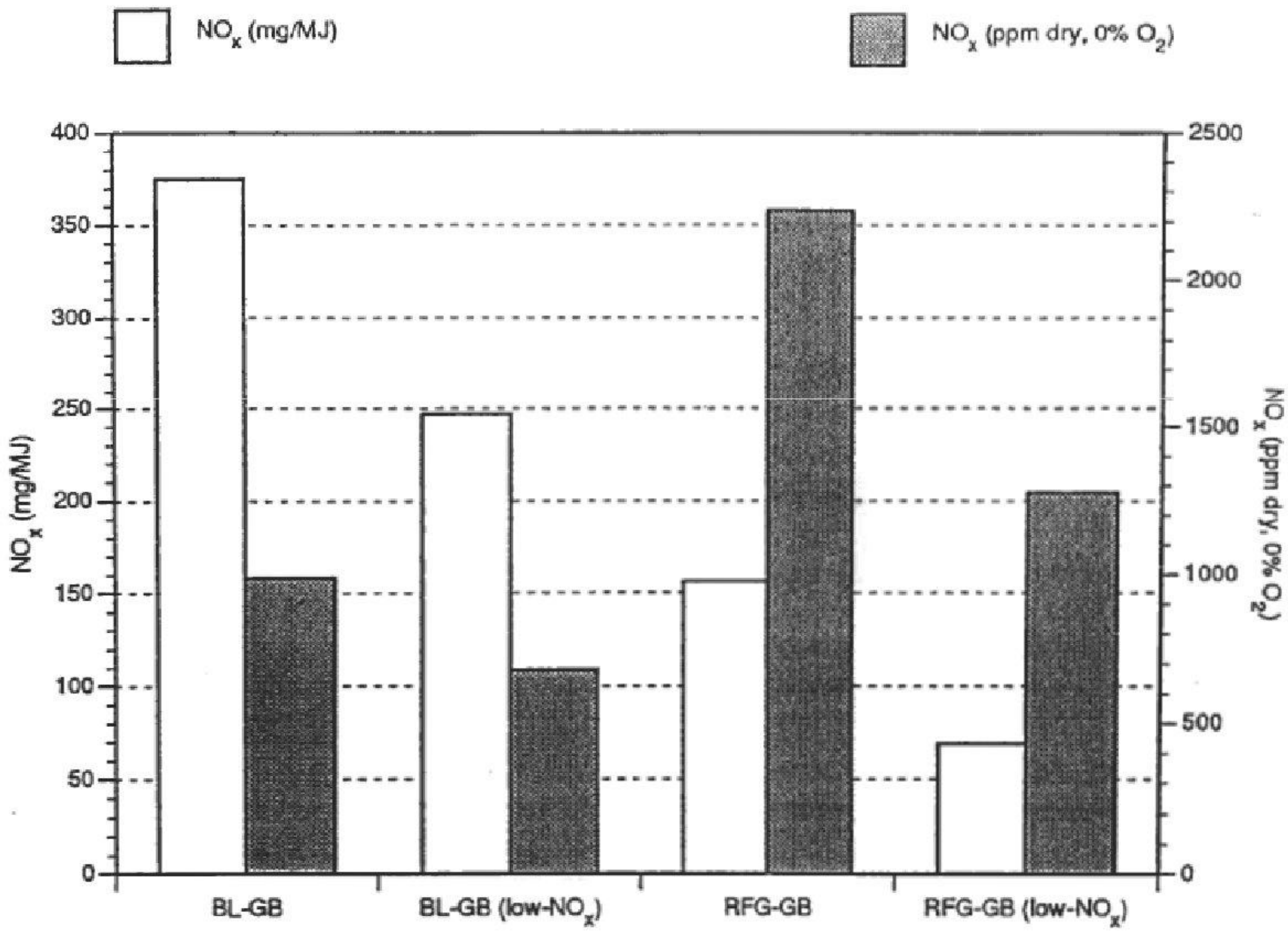




Results from IFRF study (APG4)



来自IFRF的研究结果(APG4)



SO_2 Emissions

- Highly dependent on how sulphur is captured in ash...

- without the removal of SO_2 in the secondary RFG, it should noted that a maximum of ~30% reduction could be expected (on mass per unit energy input basis)

SO_2 排放

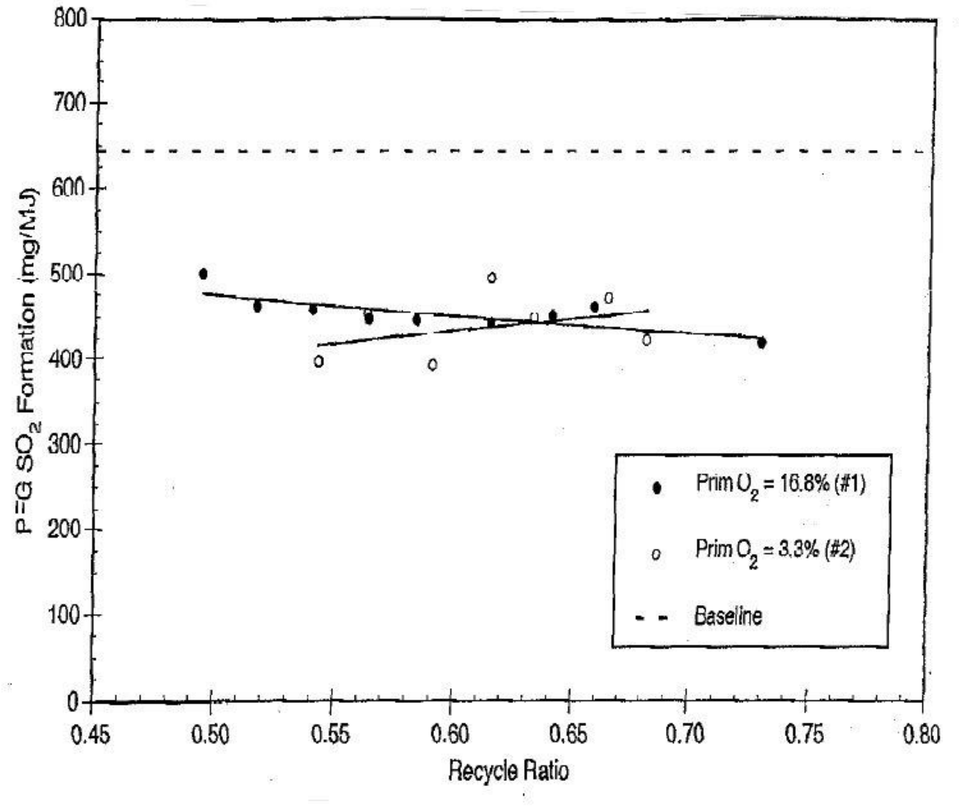
——高度依赖于如何捕集飞灰中的硫……

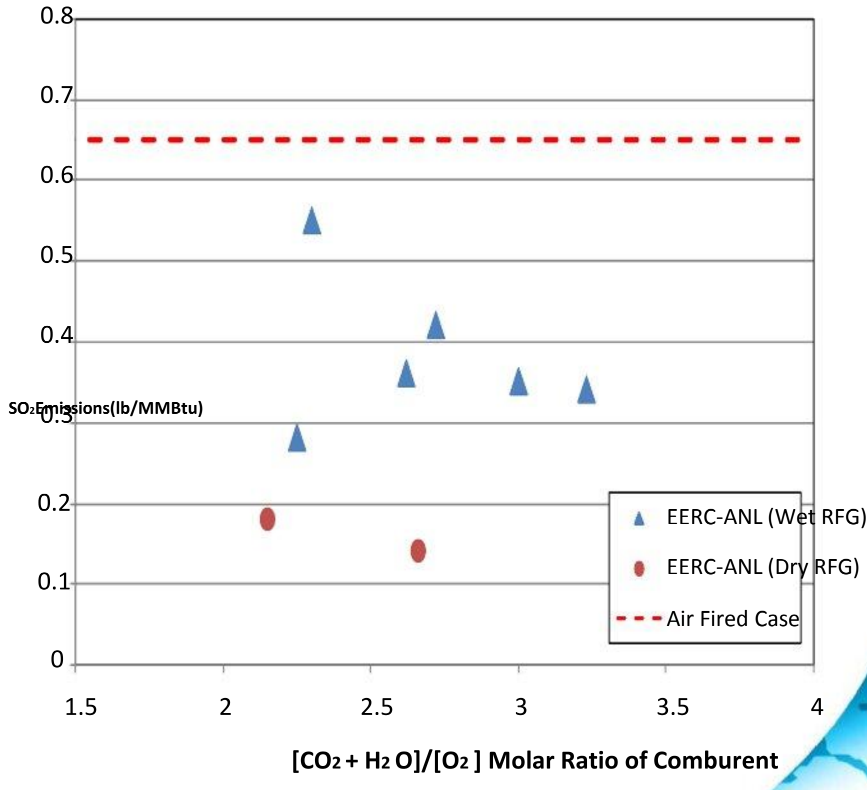
——如果不脱除二次循环烟气中的SO_2，预计将高达约30%的脱硫率

(单位能量输入对应的质量)

SO_2 Emissions

(Results from ANL-EERC and IFRF)





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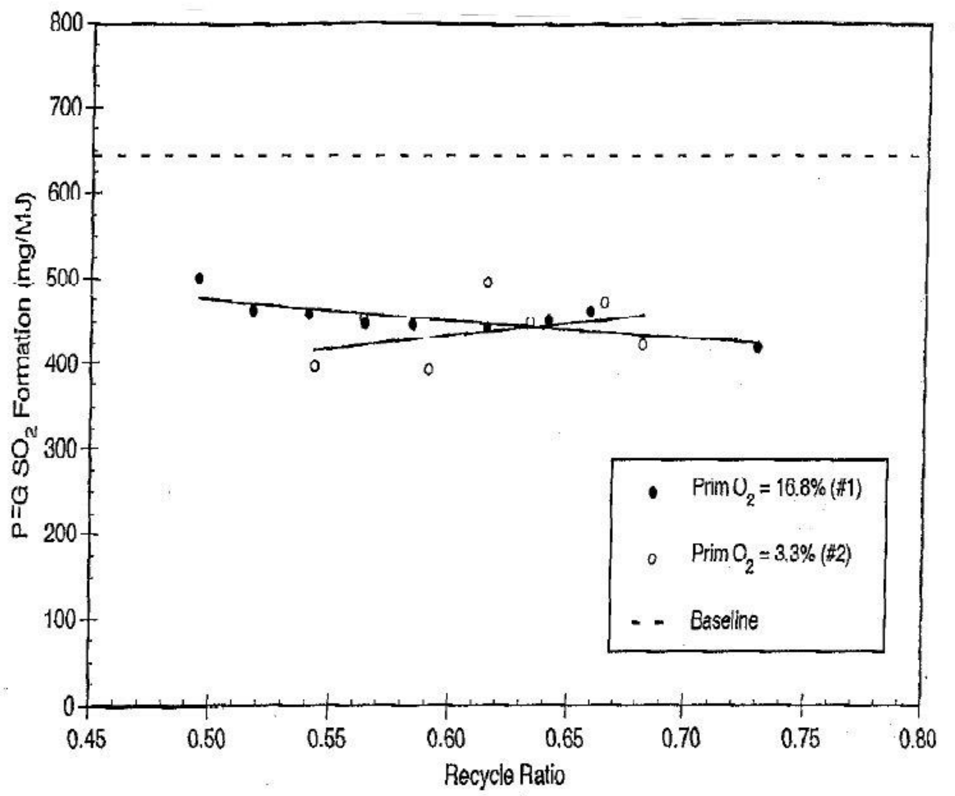
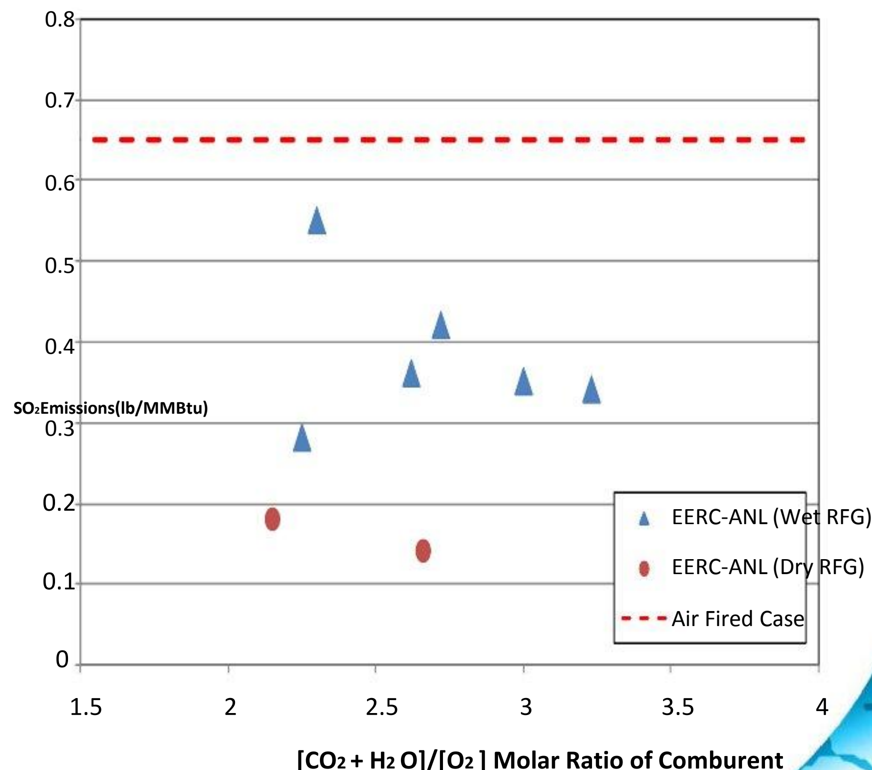
SO_2排放

(结果来自ANL-EERC和IFRF)





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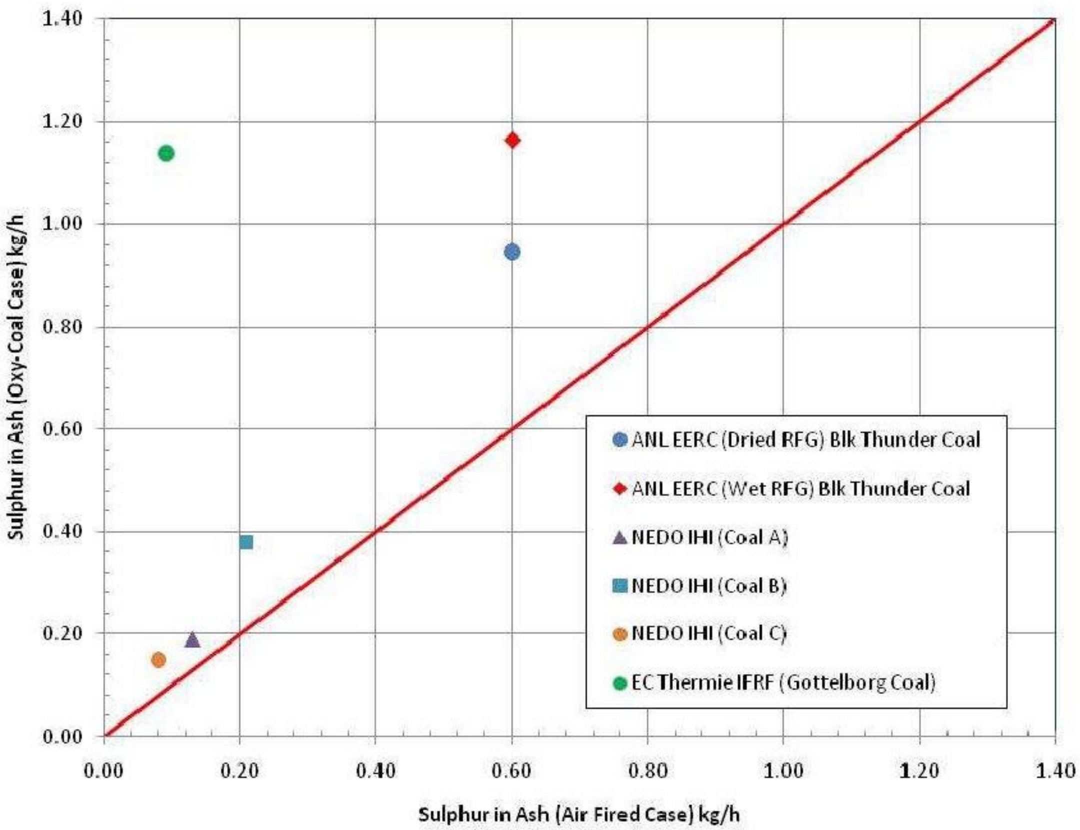
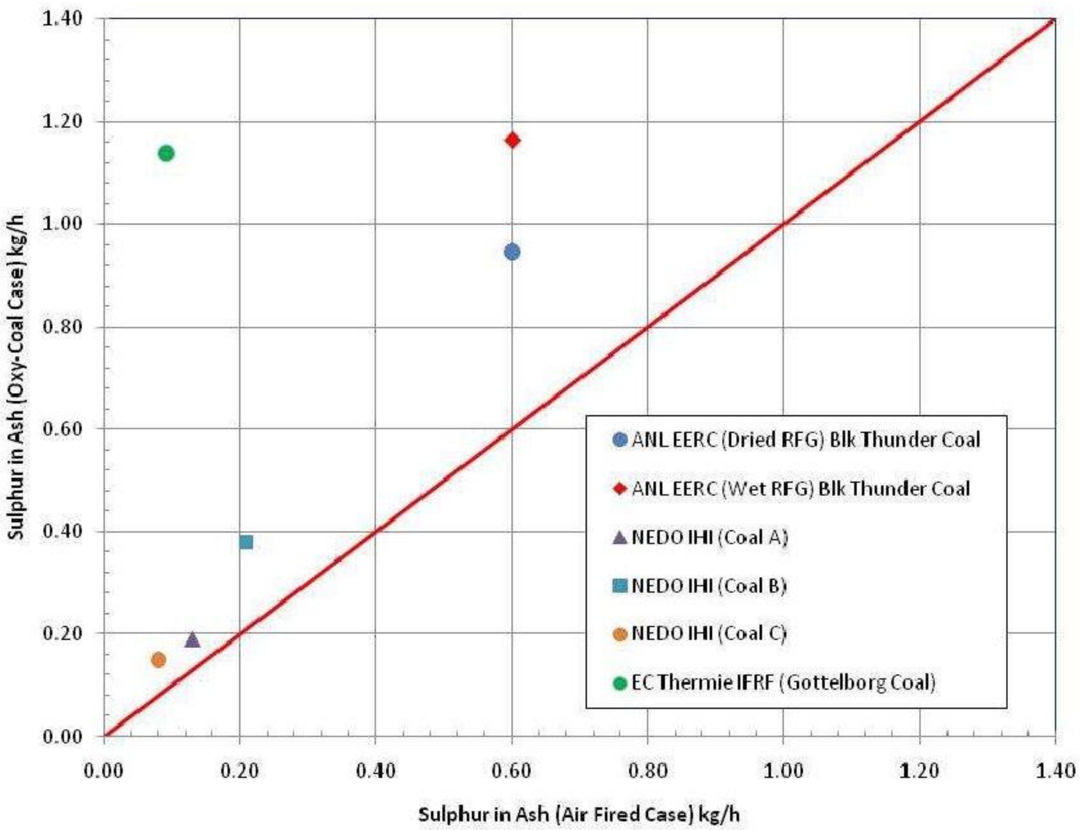
Sulphur in ash



24

飞灰含硫量



1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Sulphur in Ash (Oxy-Coal Case) kg/h
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
Sulphur in Ash (Air Fired Case) kg/h
ANL EERC (Dried RFG) Blk Thunder Coal
ANL EERC (Wet RFG) Blk Thunder Coal
NEDO IHI (Coal A)
NEDO IHI (Coal B)
NEDO IHI (Coal C)
EC Thermie IFRF (Gottelborg Coal)

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Fundamental question in attempt to explain the reduction of SO_2…

- ***Reduction of SO_2 under oxy-coal combustion conditions - Could this observations due to 2 competing phenomena in the furnace and in the convective section???***
  - High temperature sulfation of the ash (as proposed by Okazaki et. al.) - which could be in agreement base on the data of IFRF (APG2 Trials).
  - Sulfur capture in ash at convective section enhanced by higher SO_3 formation, higher deposition rate and lower carbon in ash.

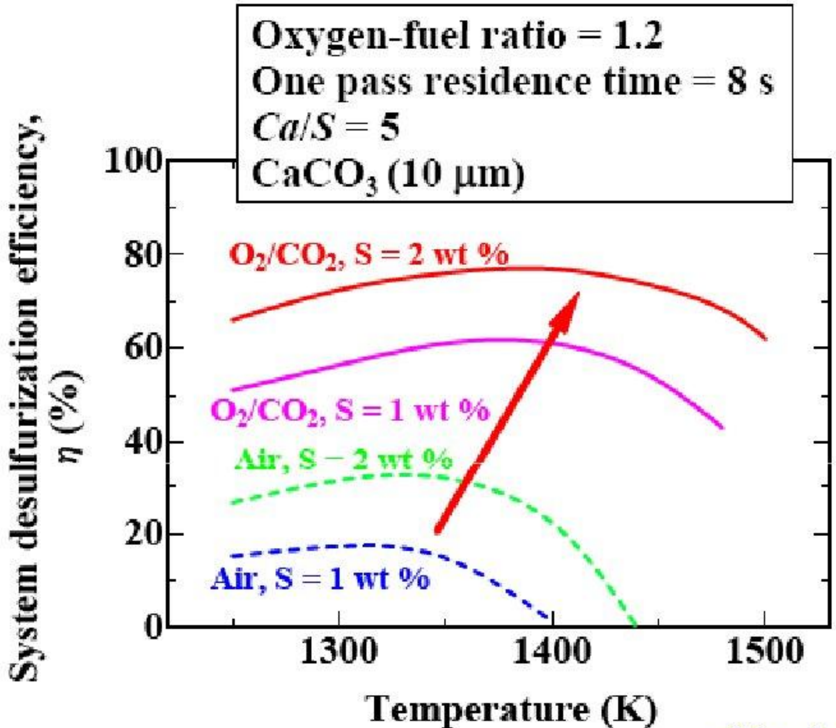
如何解释SO_2减排的基本问题……

- ***燃煤富氧燃烧条件下SO_2的减排***
  ——这个现象能归结于炉膛及对流烟道两个因素的共同作用吗???

  - 飞灰高温硫酸盐化(正如Okazaki 等提出的)
    ——这与 IFRF (APG2 试验)数据一致

  - 由于对流烟道SO_3含量高、沉积速率快、飞灰含碳量低，硫的捕集效果得到增强

Drastic Enhancement of In-furnace Desulfurization Efficiency



η at S = 1 wt %
six times higher

In-furnace desulfurizatioin at high temperature

Air: impossible

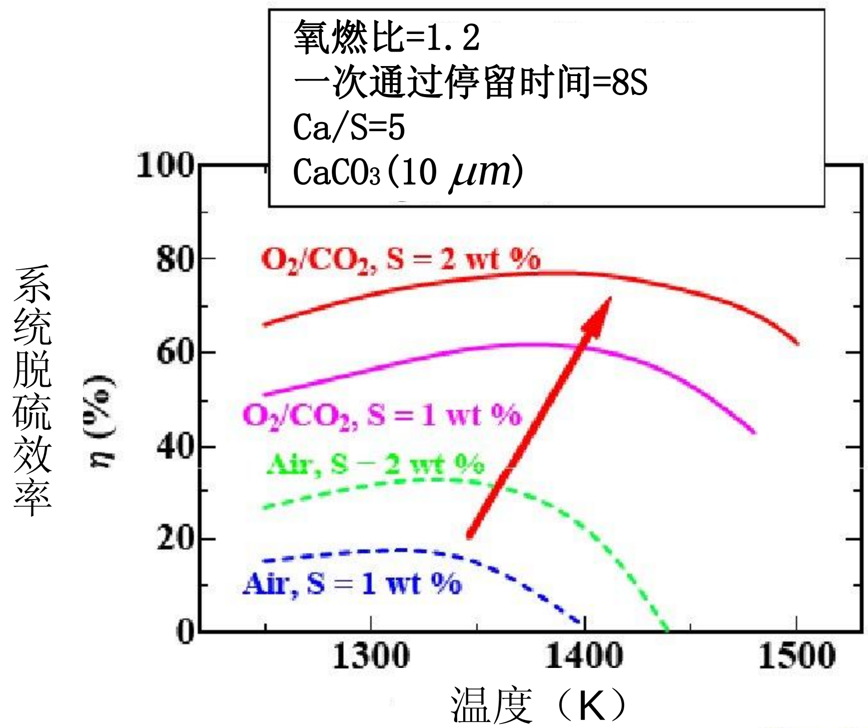
O_2/CO_2: can be realized

<Liu & Okazaki, EERGY & FUEL, 2001>

η in O_2/CO_2 ➡ about four times higher
➡ high in a wide temperature range

Effect of temperature on system desulfurization efficiency

炉内脱硫效率的显著增强



S=1wt%时

η 升高六倍

高温下

炉内

脱硫

空气：无法实现

O_2/CO_2：

可以实现

<*Liu & Okazaki, EERGY & FUEL, 2001*>

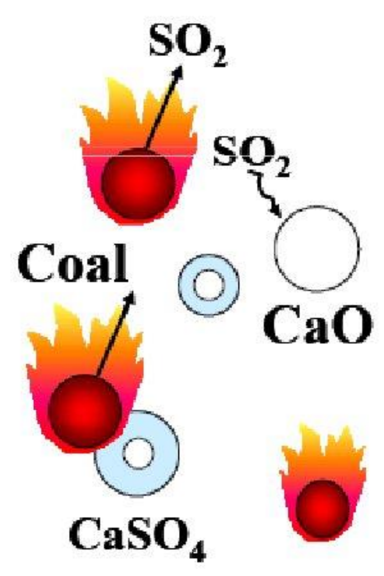
O_2/CO_2中η ⇒ 升高四倍
⇒ 在较宽的温度范围内高

温度对系统脱硫效率的影响

Mechanism of In-furnace Desulfurization

What is in-furnace desulfurization? → A very economical method of SO_2 removal through sorbent ($CaCO_3$) injection into the furnace

<Liu & Okazaki, EERGY & FUEL, 2001>



Desulfurization reaction:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + SO_2 + 1/2O_2 \rightarrow CaSO_4$$

$CaSO_4$ decomposition:

$$CaSO_4 \rightarrow CaO + SO_2 + 1/2O_2$$

The cause of decrease in desulfurization efficiency at high temperature

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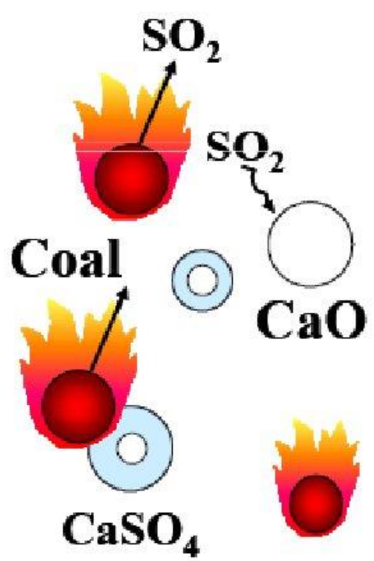
炉内脱硫机理

什么是
炉内脱硫

一种经济的SO_2脱除方法，
通过向炉内喷入吸收剂$CaCO_3$

<*Liu & Okazaki, EERGY & FUEL, 2001*>



脱硫反应：

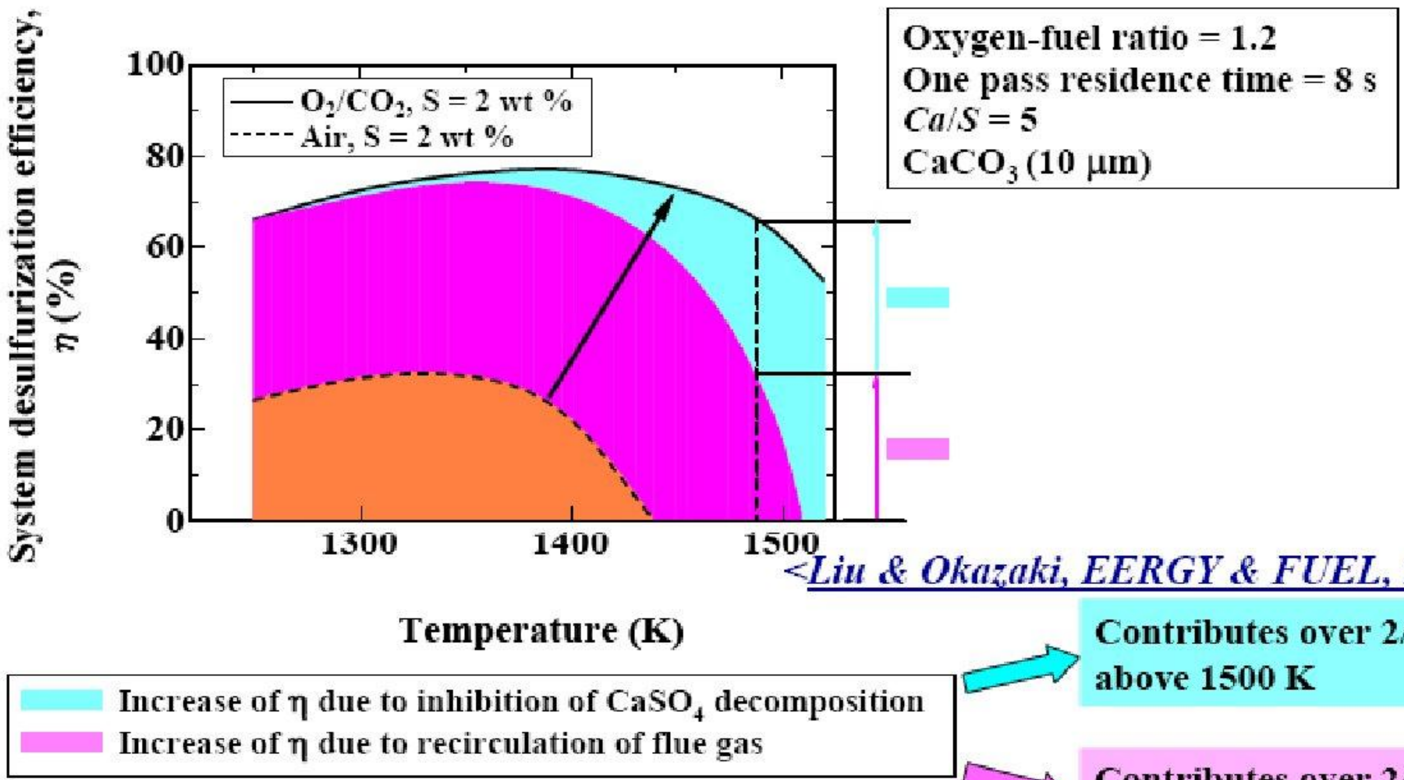
$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + SO_2 + 1/2O_2 \rightarrow CaSO_4$$

$CaSO_4$ 分解：

$$CaSO_4 \rightarrow CaO + SO_2 + 1/2O_2$$

高温区脱硫
效率降低的原因



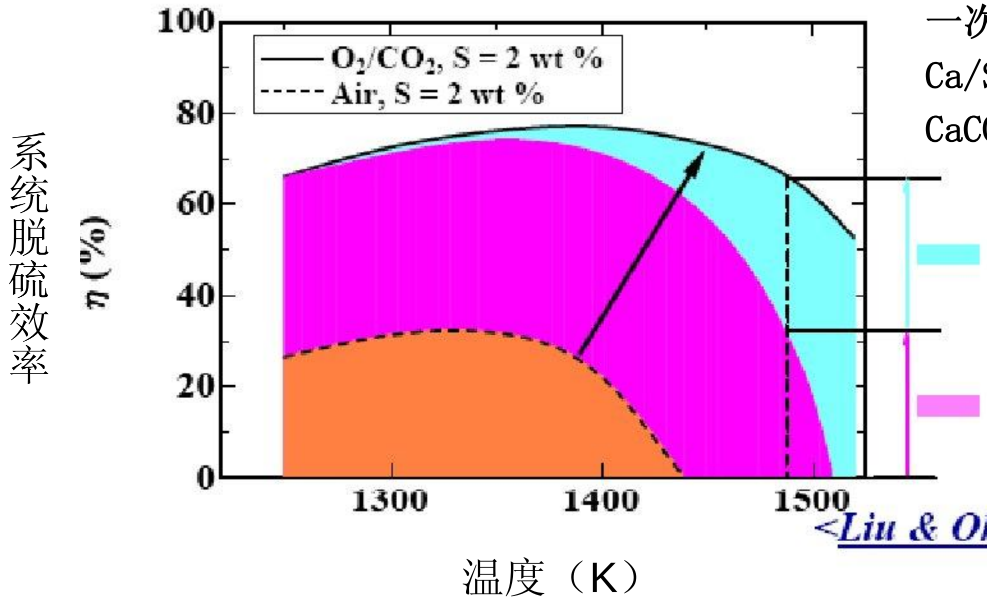
<Liu & Okazaki, EERGY & FUEL, 2001>

Contributes over 2/3 above 1500 K

Contributes over 2/3 below 1450 K

Contributions of different factors to the increase in system desulfurization efficiency

氧燃比=1.2
一次通过停留时间=8S
Ca/S=5
$CaCO_3$(10 μm)



<u><*Liu & Okazaki, EERGY & FUEL, 2001*></u>

- $CaSO_4$分解的抑制使 η增加
- 烟气再循环使η 增加

1500K以上时，
超过**2/3**的贡献

1450K以下时，
超过**2/3**的贡献

系统脱硫效率增加的不同因素的贡献

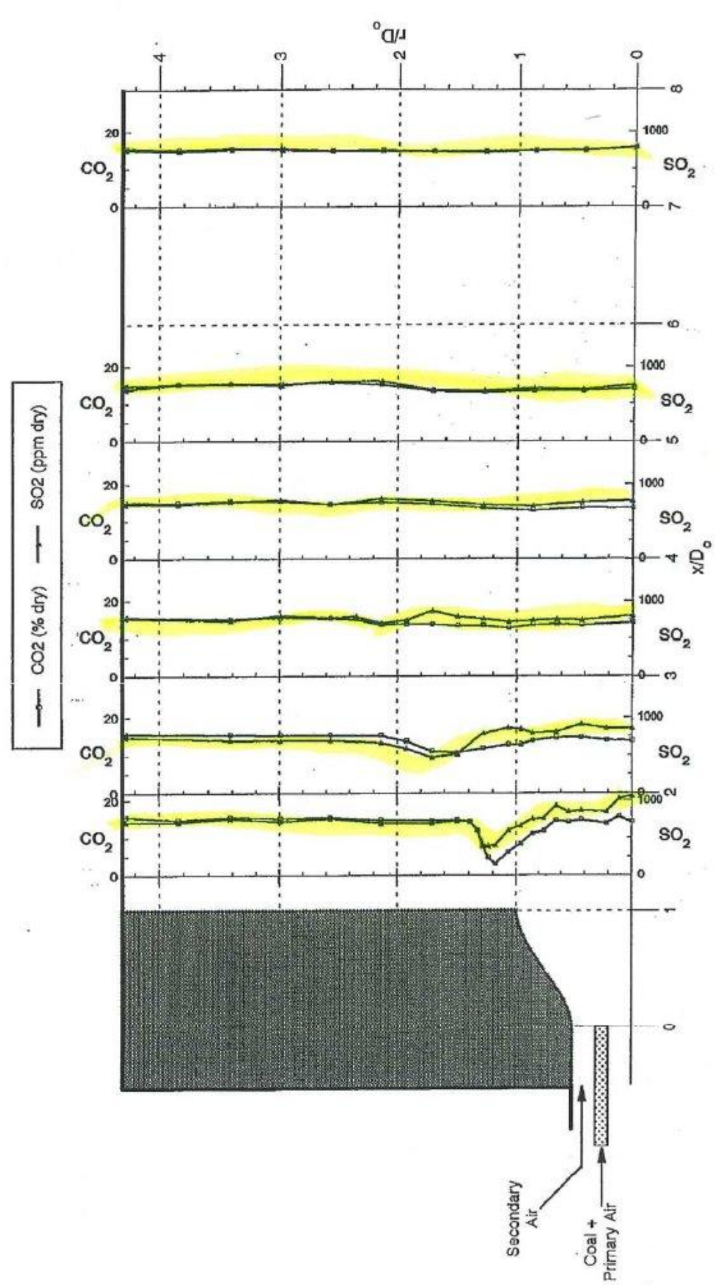


Figure 6-4 In-Flame Carbon Dioxide and Sulfur Dioxide Profiles (baseline flame)

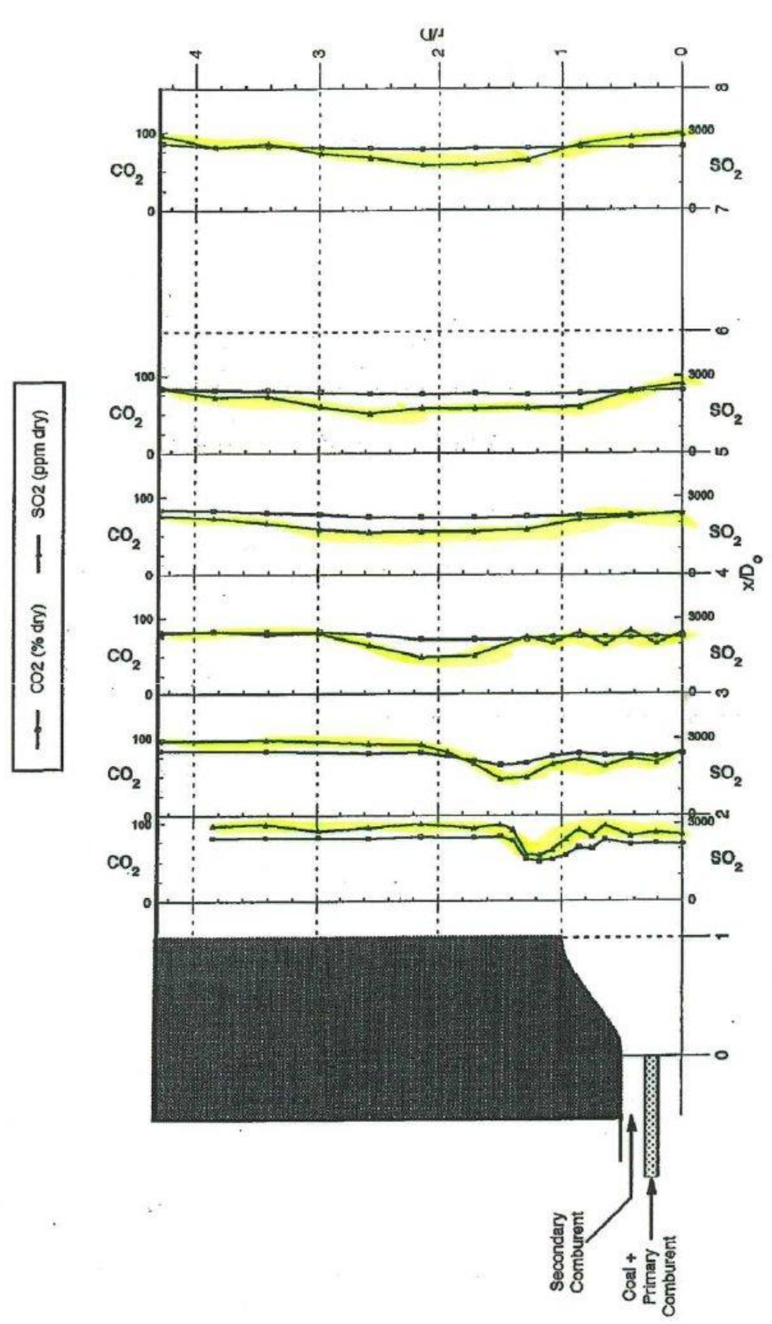


Figure 6-14 In-Flame Carbon Dioxide and Sulfur Dioxide Profiles (Flame C - optimum firing condition)

Results from IFRF study (APG2)

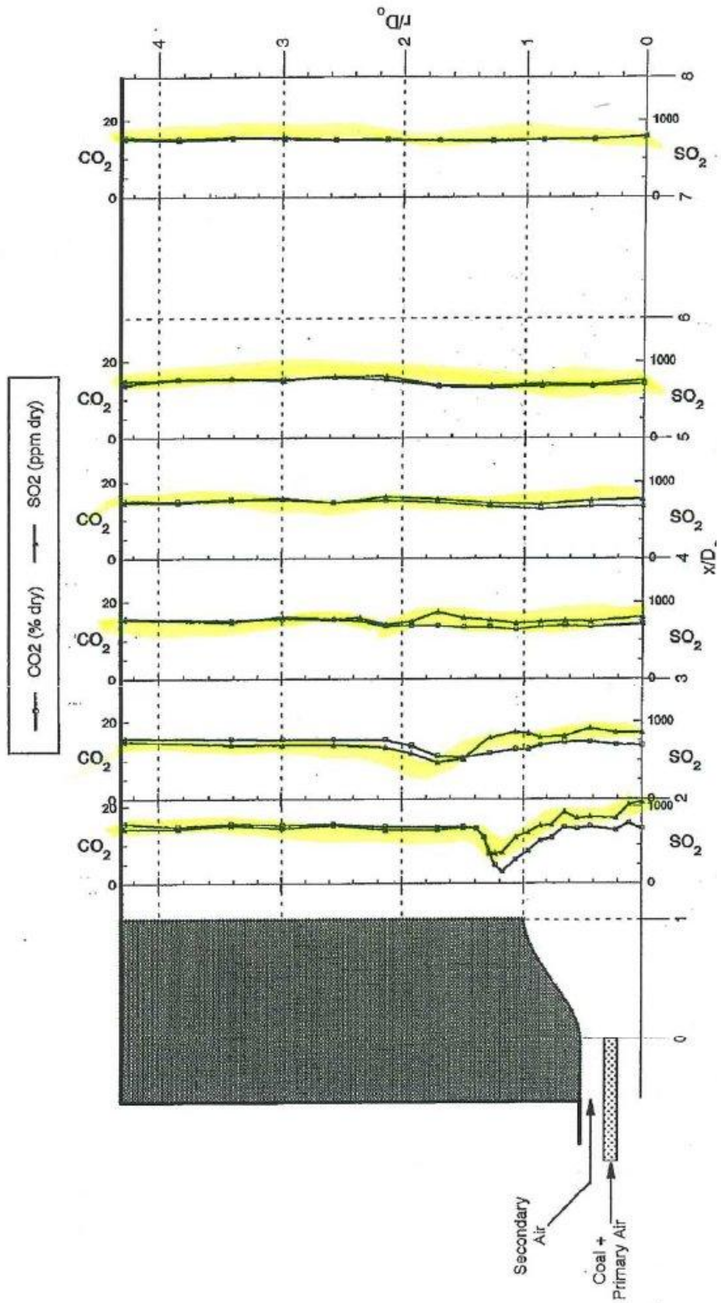


图6-1 炉内二氧化碳和二氧化硫分布

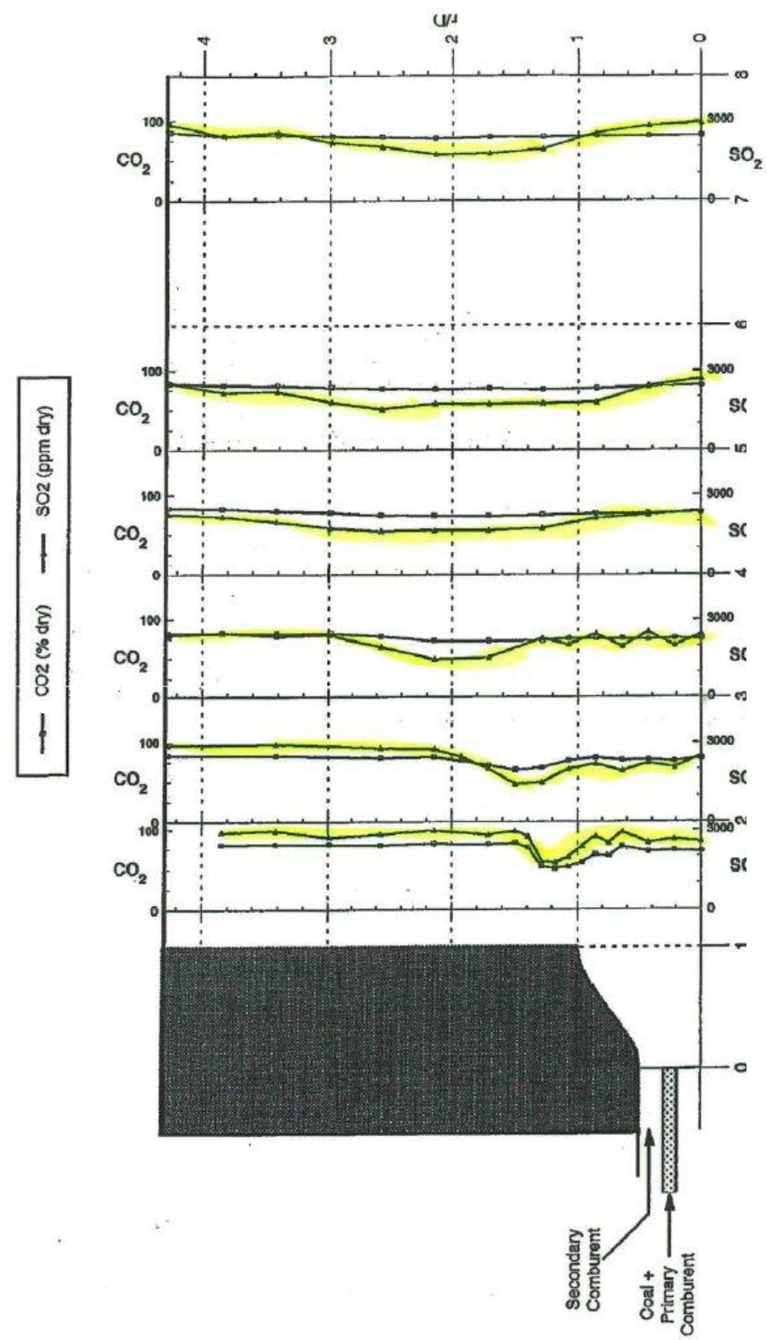


图6-14 炉内二氧化碳和二氧化硫分布（图C最佳着火条件）

IFRF研究结果（APG2）

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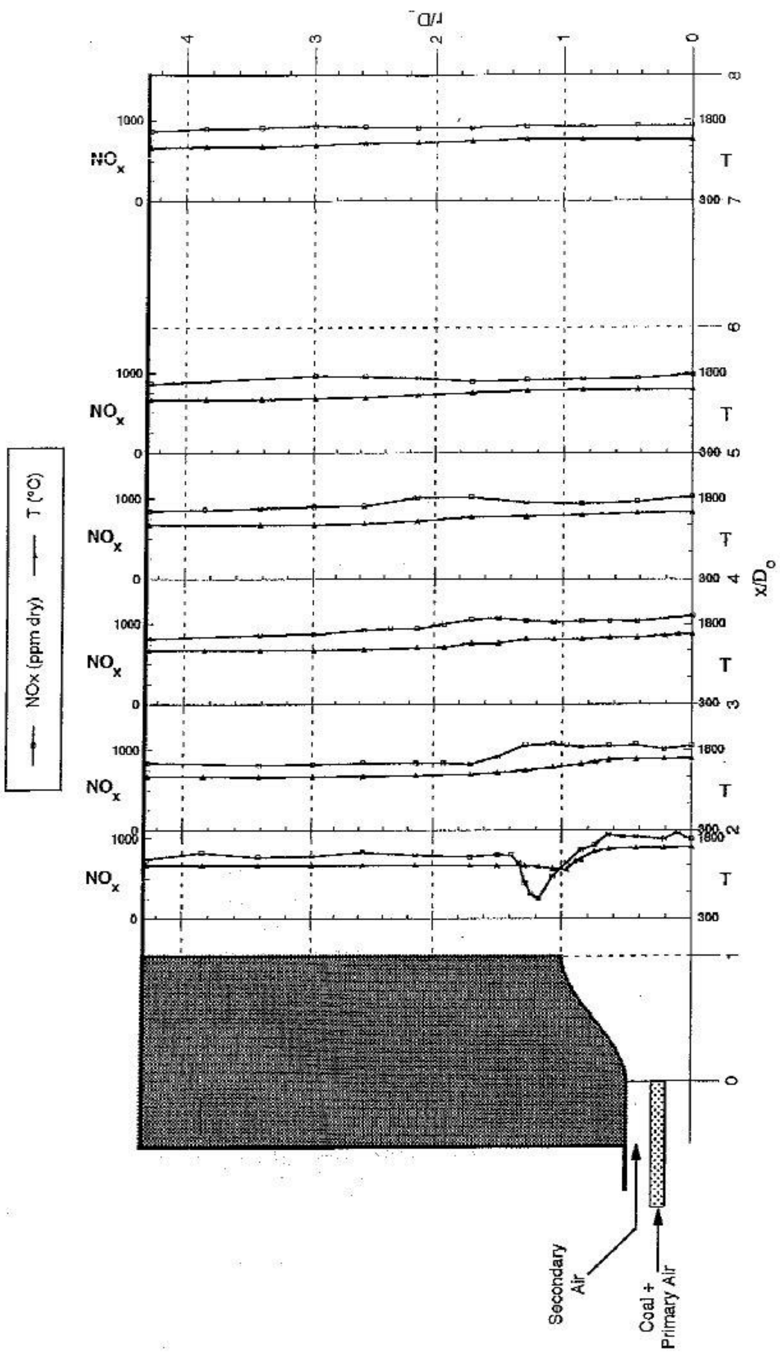


Figure 6-5 In-Flame NO_x and Temperature Profiles (baseline flame)

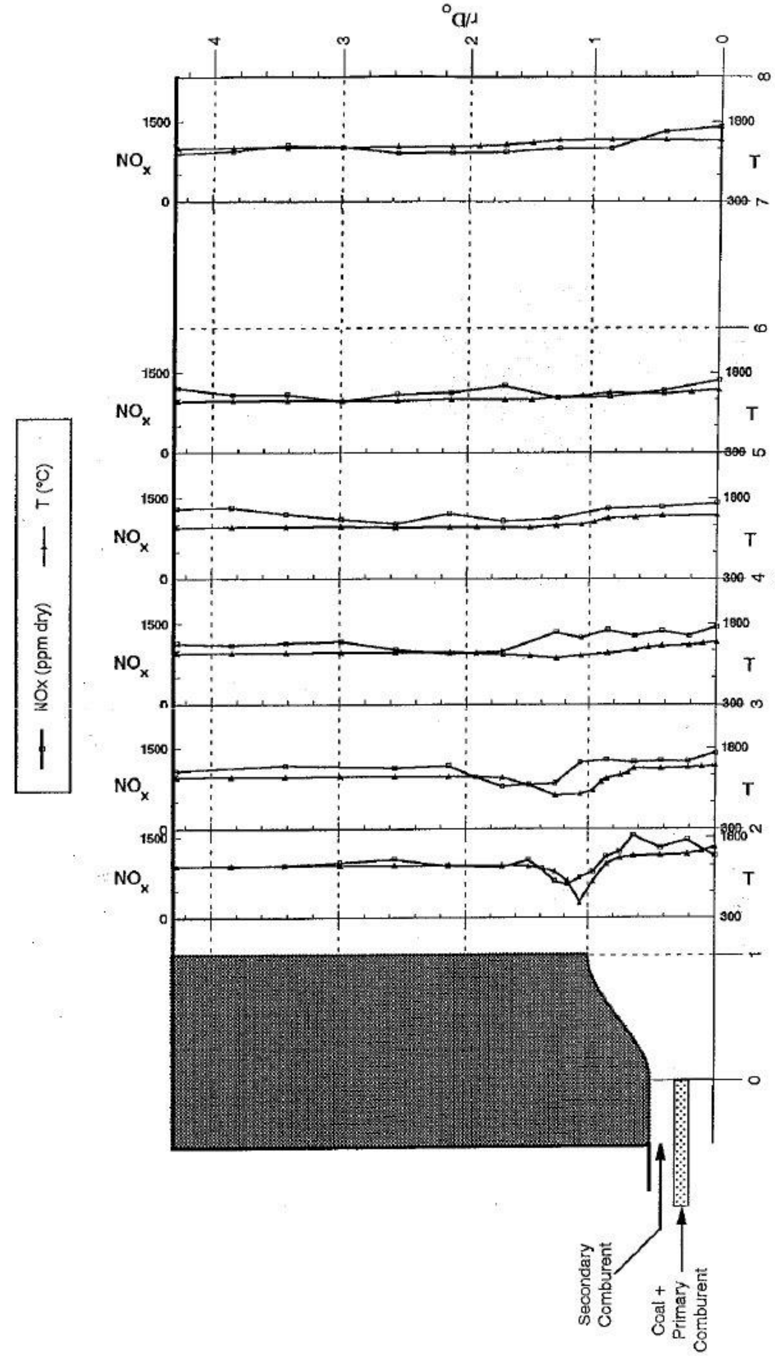


Figure 6-15 In-Flame NO_x and Temperature Profiles (Flame C - optimum firing condition)

Results from IFRF study (APG2)

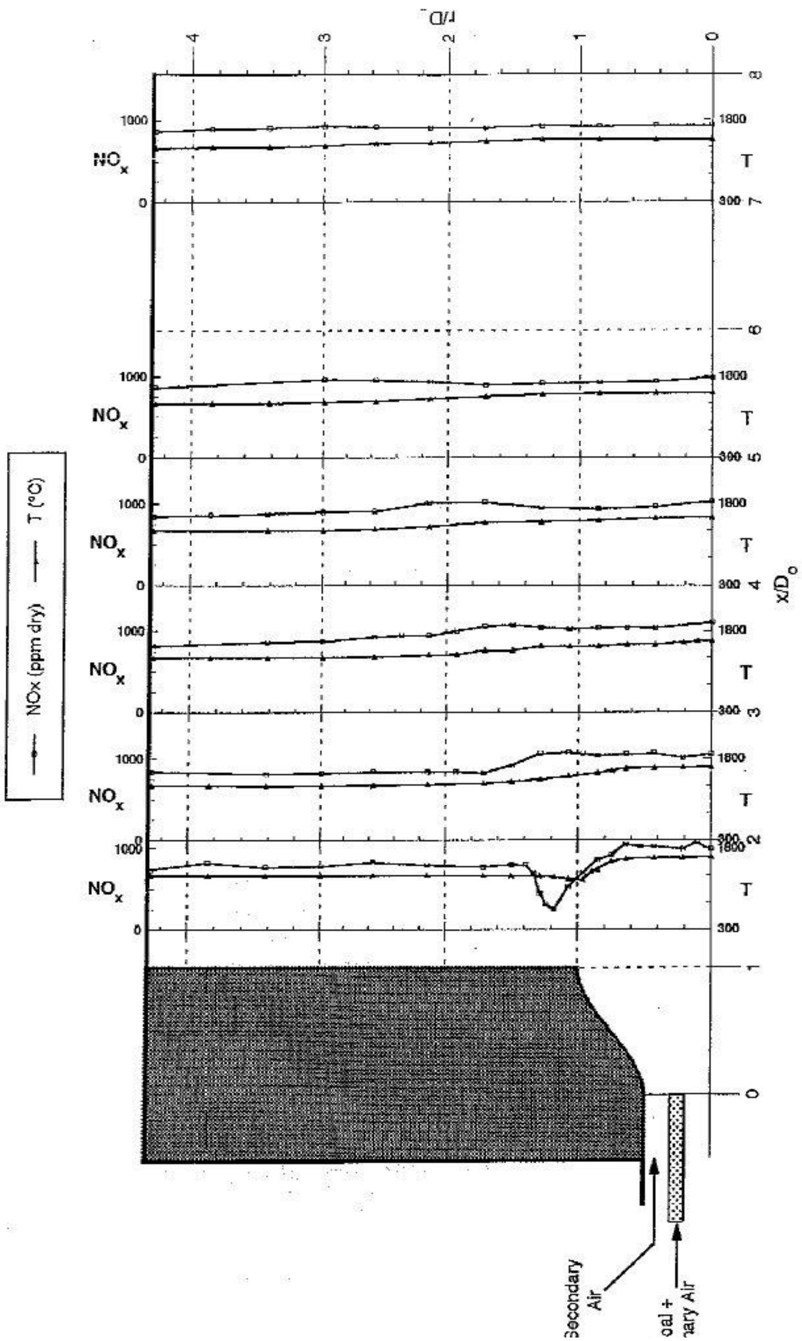


图6-5 炉内NOx和温度分布（最佳火焰）

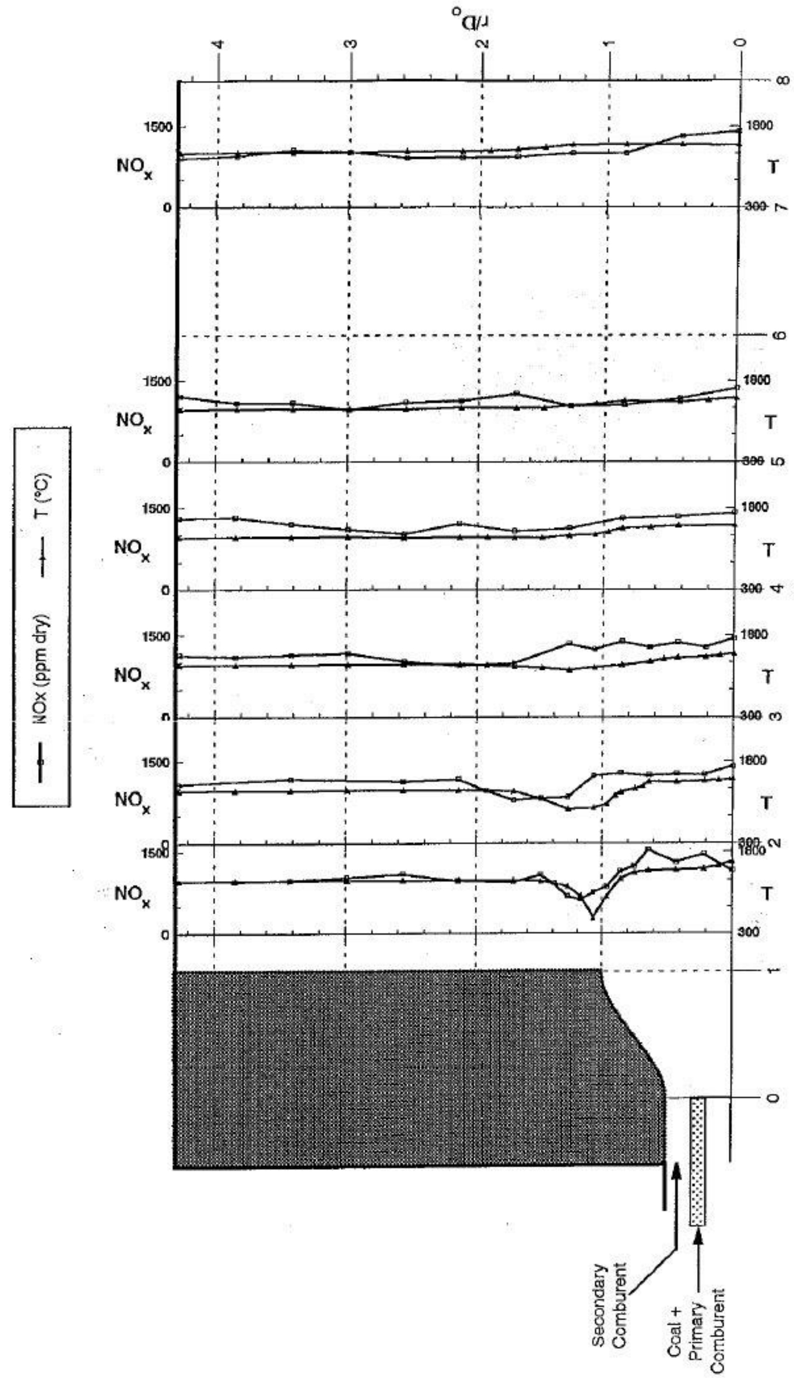


图6-15 炉内NOx和温度分布（图C 最佳着火条件）

IFRF研究结果（APG2）

Issue of SO_3

- The confirmation of the ANL results as presented from the results of IVD Stuttgart, IHI/Calide Project, Vattenfall, Chalmers University.

- Nonetheless, there are still a lot of confirmation to be done!!!

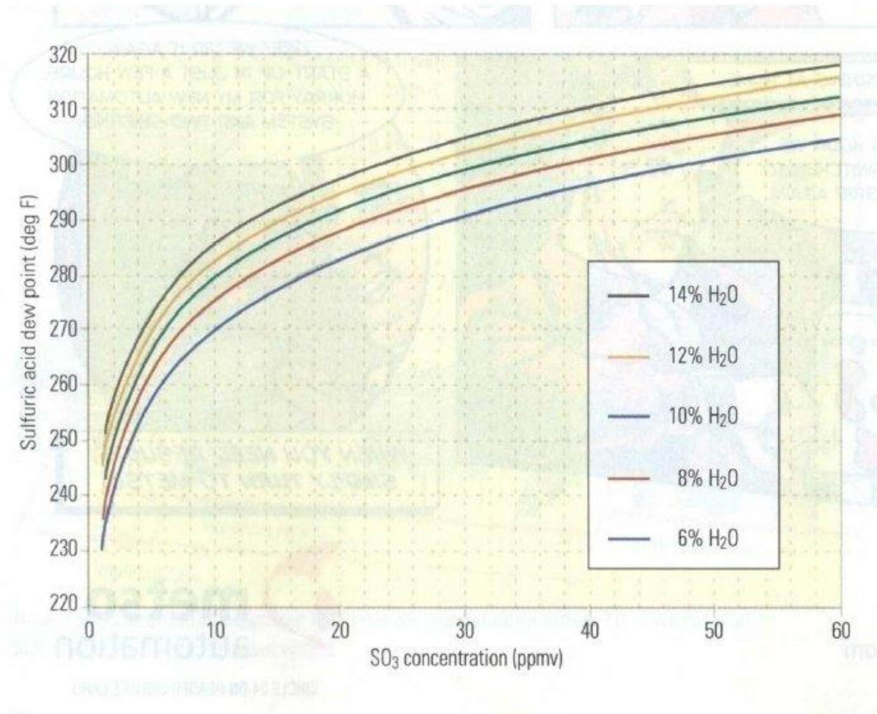
SO_3问题

——IVDStuttgart、IHI/Calide项目、Vattenfall,查尔姆斯大学确认了ANL的研究结果。

——但是，仍有很多问题需要解决!!!

Oxy-Combustion: KEY ISSUES

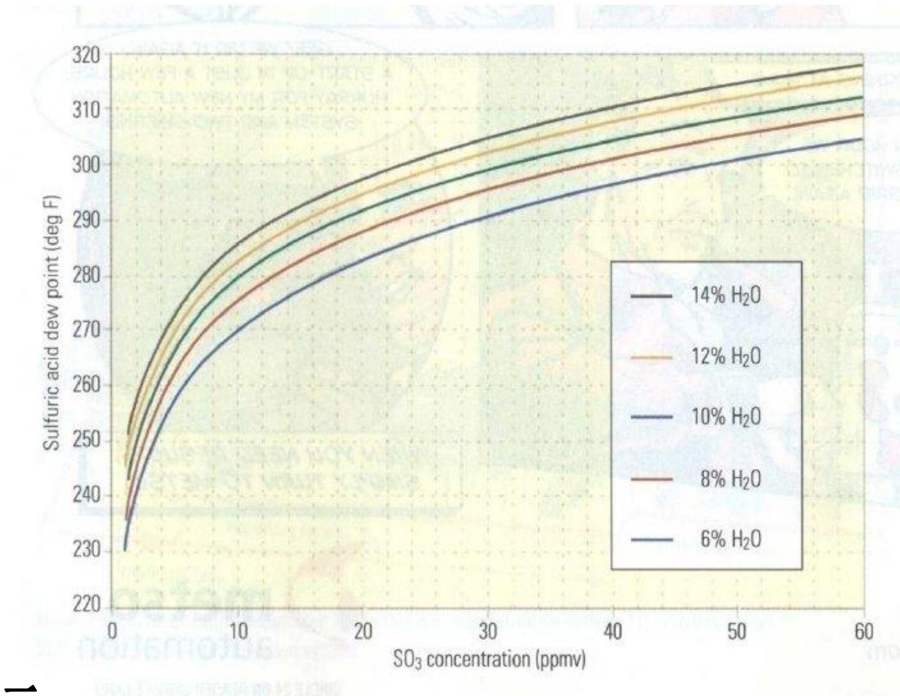
- ***SO_3 issue is a big missing link! (4 years ago)***
- ***ANL study (1985) have indicated that SO_3 formation is 3 to 5 times greater as compared to conventional air – firing mode***
- ***We need to know more about the potential operational issue.***



From Chemical Engineering Progress (Vol. 70)

富氧燃烧: 关键问题

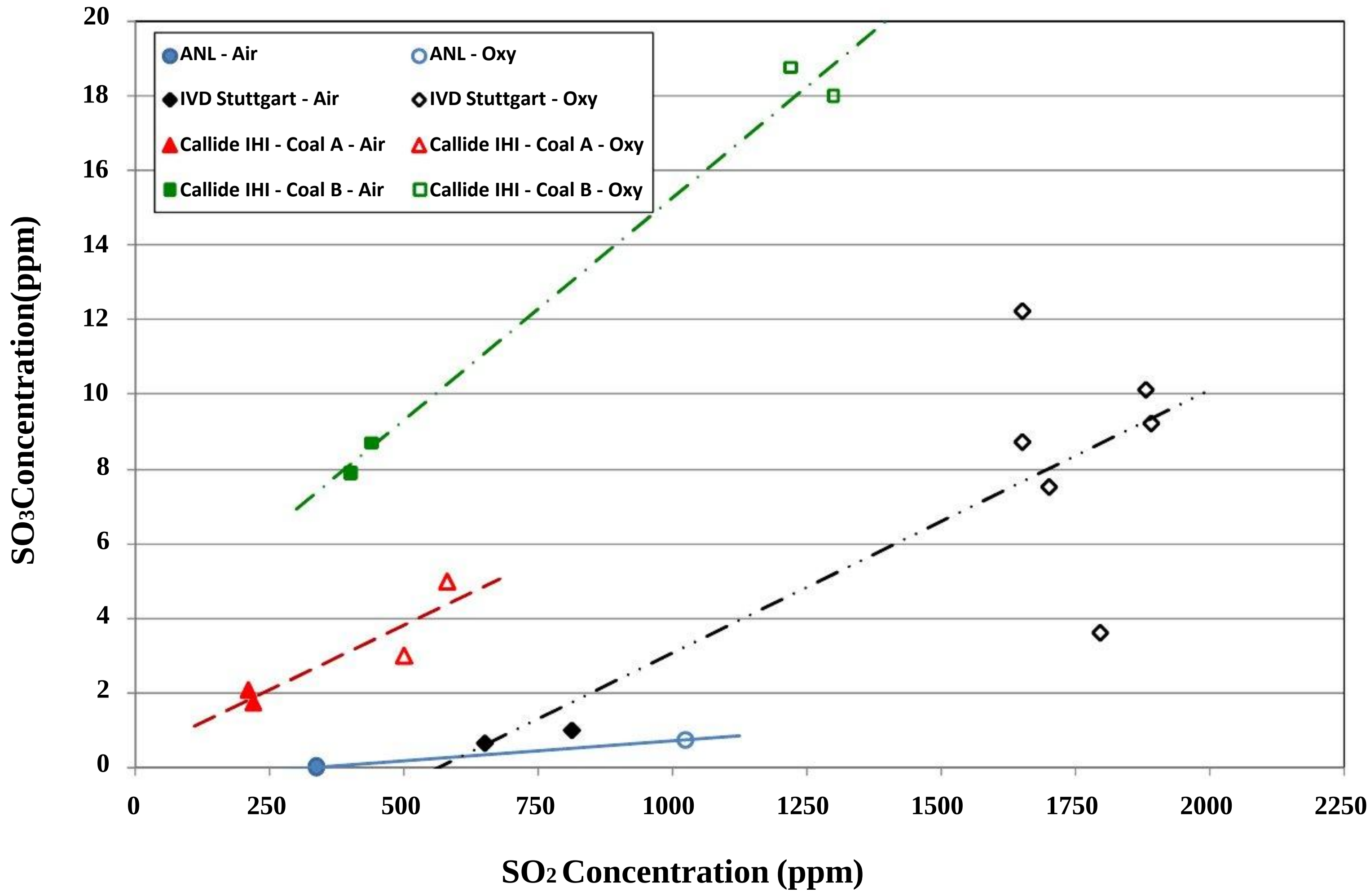
- *四年前SO_3 问题是被忽视的环节！*
- ***1985年ANL研究表明：SO_3的浓度比常规空燃模式高3~5倍***
- *我们需要了解更多的潜在运行问题*



来自Chemical Engineering Progress (Vol. 70)

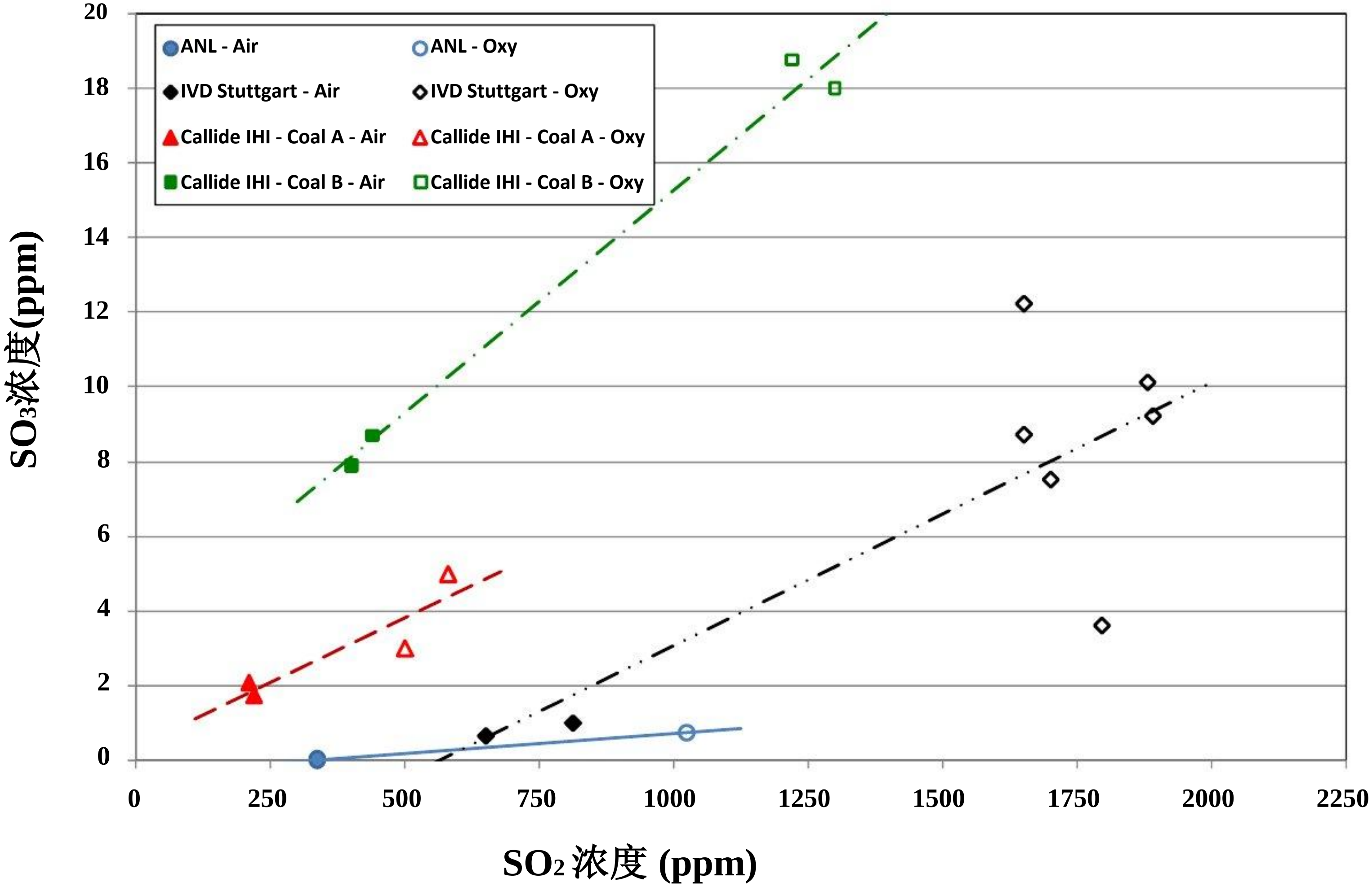
SO_3 Emissions

(Results from ANL-EERC, IVD Stuttgart, Callide/IHI)



SO_3排放

(结果来自ANL-EERC, IVD Stuttgart, Callide/IHI)



My Background Analysis…

- ***SO_2 to SO_3 conversion will most likely to occur at the convective section…***

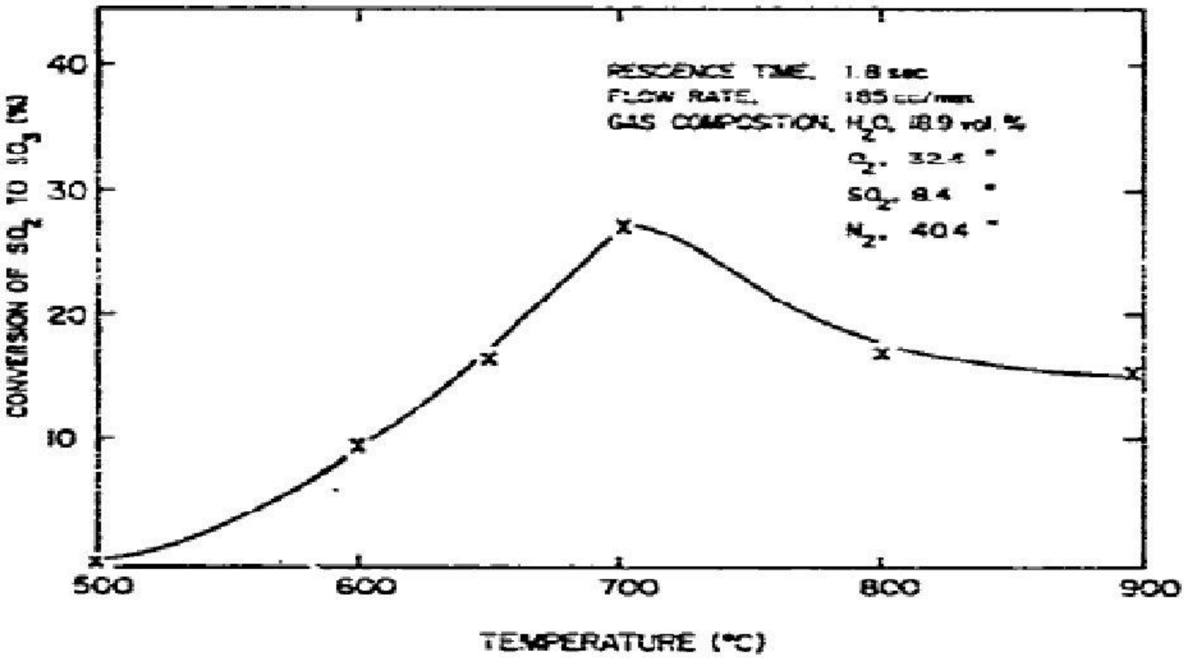


Fig. 3. Conversion of SO_2 to SO_3 in the presence of fly ash as a function of temperature.

Marrier and Dibbs (1974) Thermochmica Act (Vol. 8)

背景分析……

- ***SO_2 到SO_3 的转换过程主要在对流烟道中进行……***

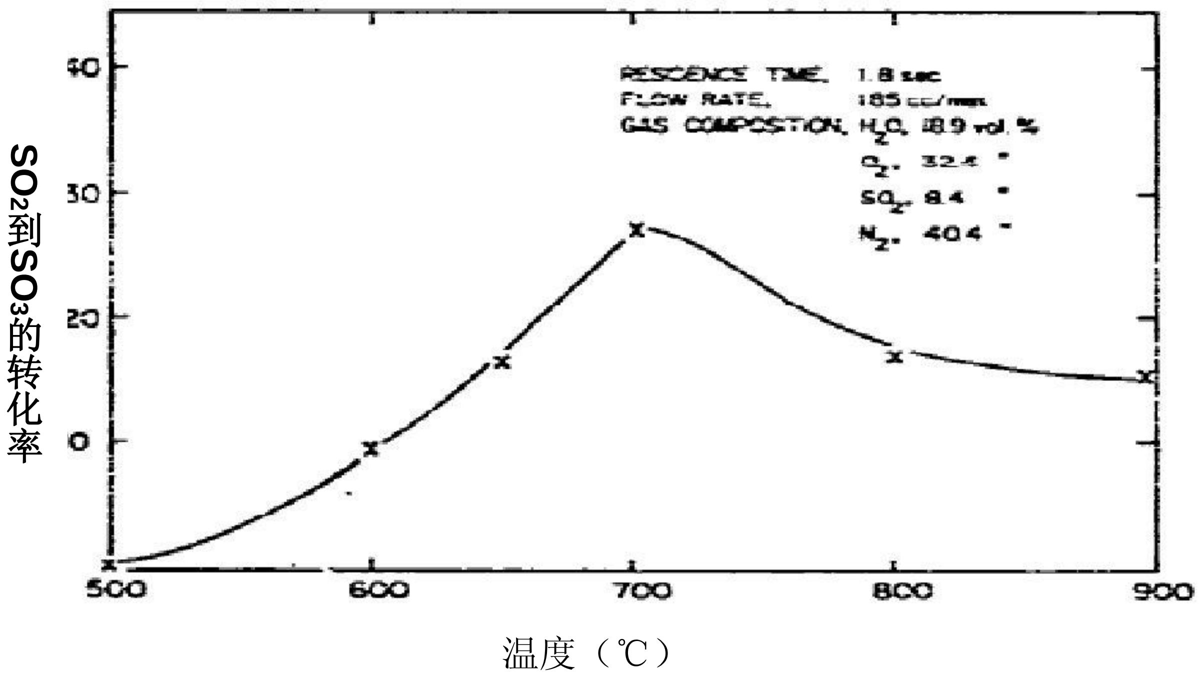


图3　飞灰中SO_2到SO_3的转化率随温度的变化

Marrier and Dibbs (1974) Thermochmica Act (Vol. 8)

SO3 formation is increased in the presence of iron oxide in the ash

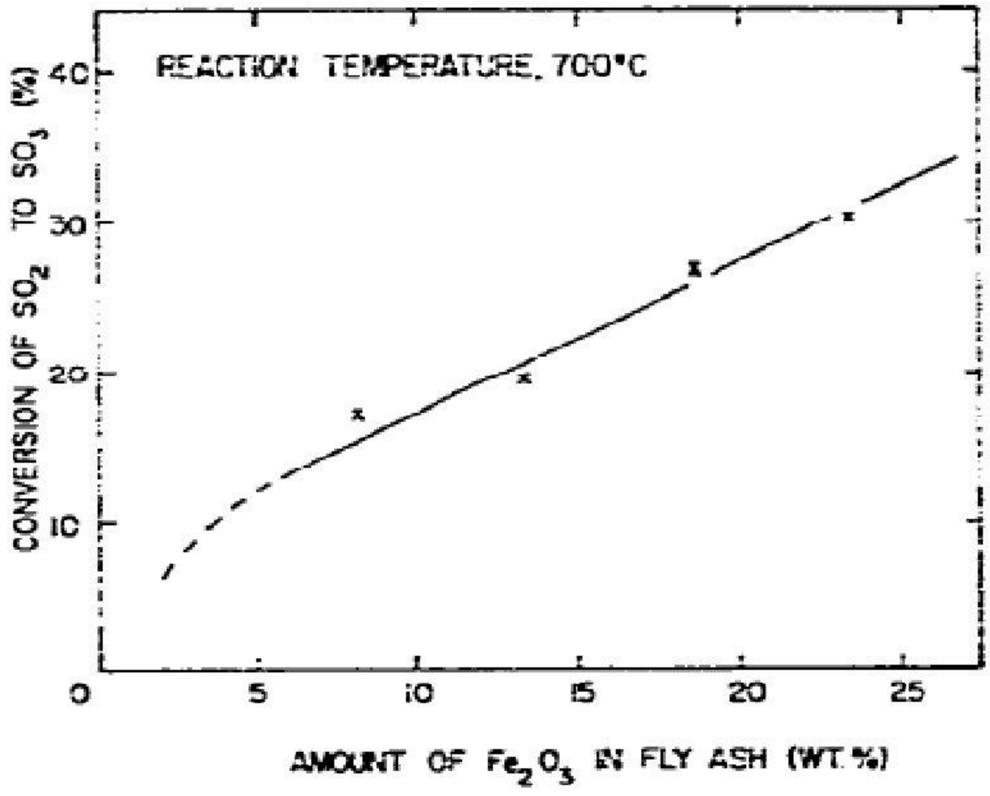
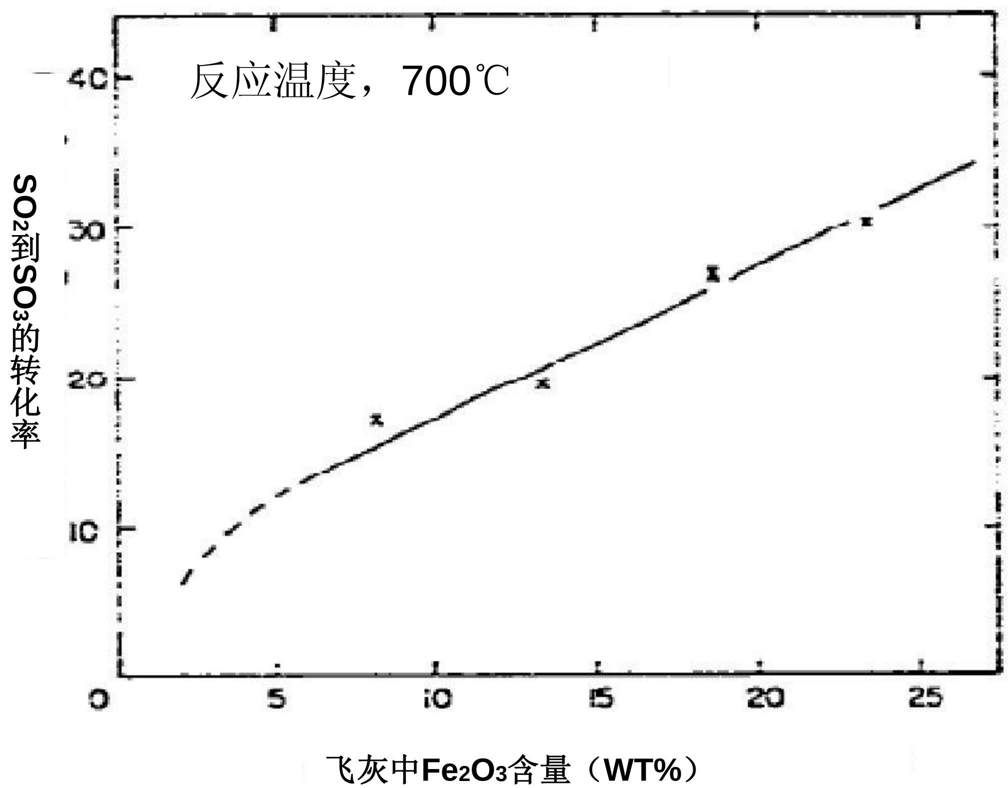


Fig. 4. Conversion of SO_2 to SO_3 at 700 °C as a function of the Fe_2O_3 content of fly ash.

Marrier and Dibbs (1974) Thermochmica Act (Vol. 8)

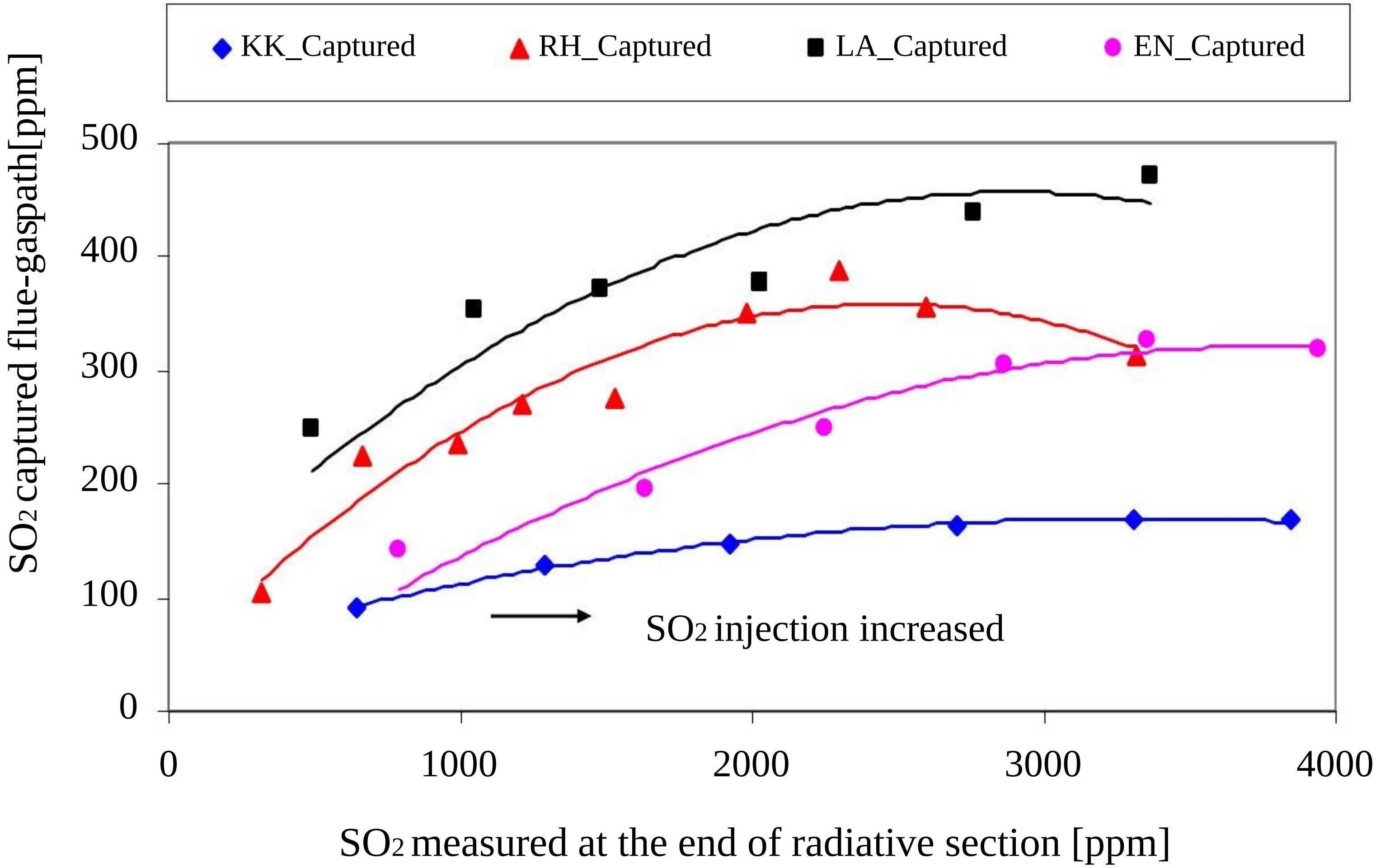
飞灰中的氧化铁使得SO_3增加



Marrier and Dibbs (1974) Thermochmica Act (Vol. 8)

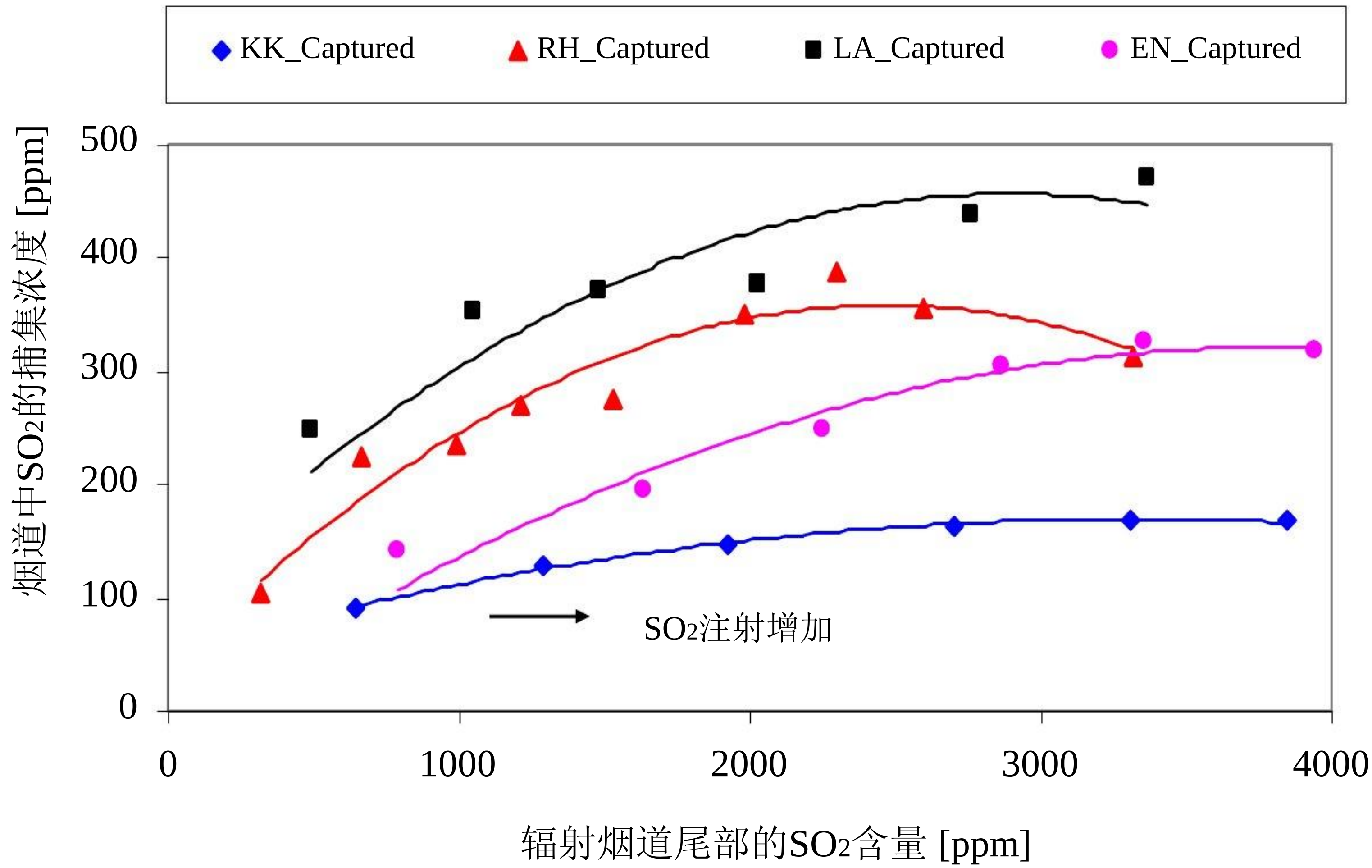
图4 700℃时SO_2到SO_3的转化率随飞灰中Fe_2O_3含量的变化

SO_2 captured along the convective part (down to 450° C) by different inlet concentrations



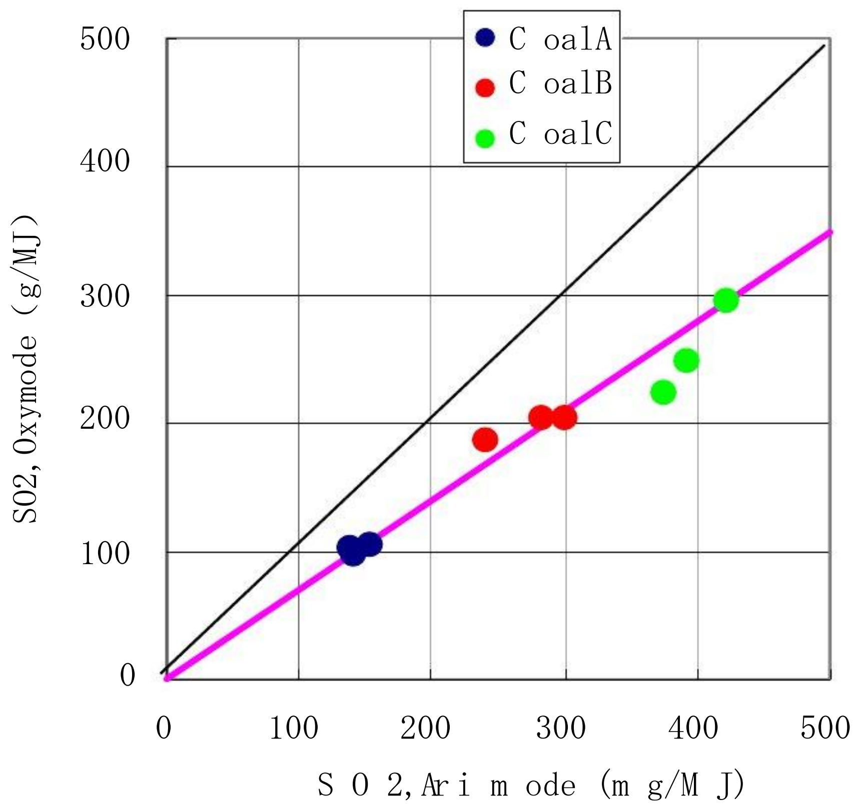
Oxy-fuel 27 % O_2

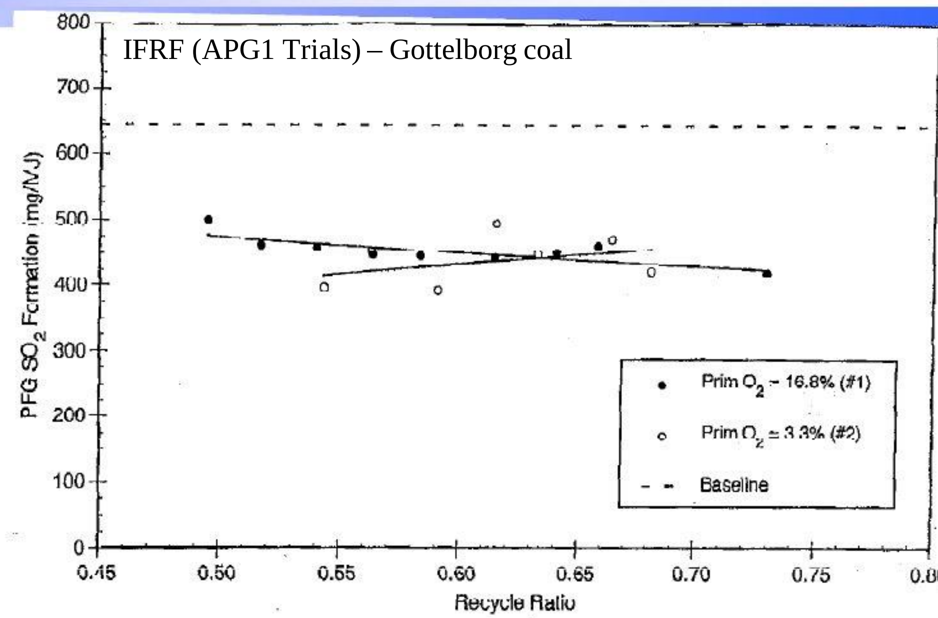
不同入口浓度下，对流烟道（低至450℃）中 SO_2 的捕集

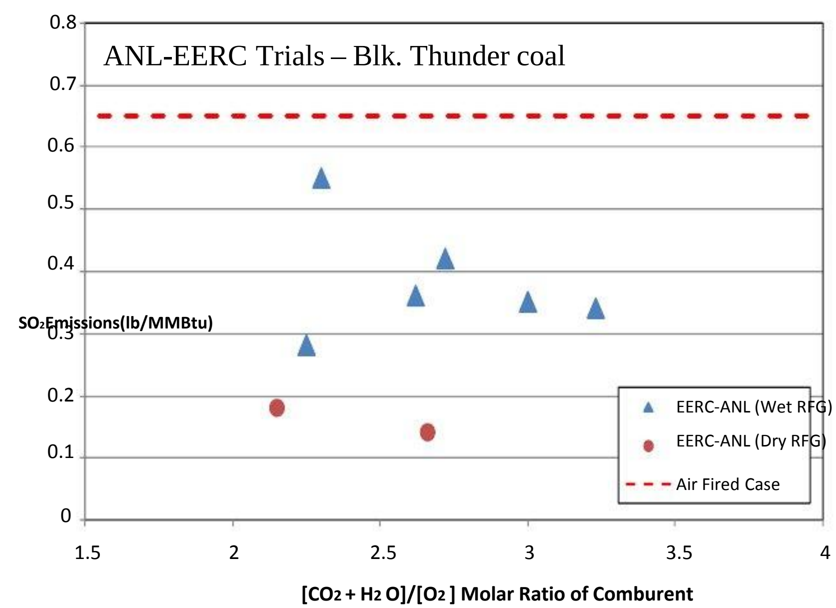


富氧燃烧 27 % O_2

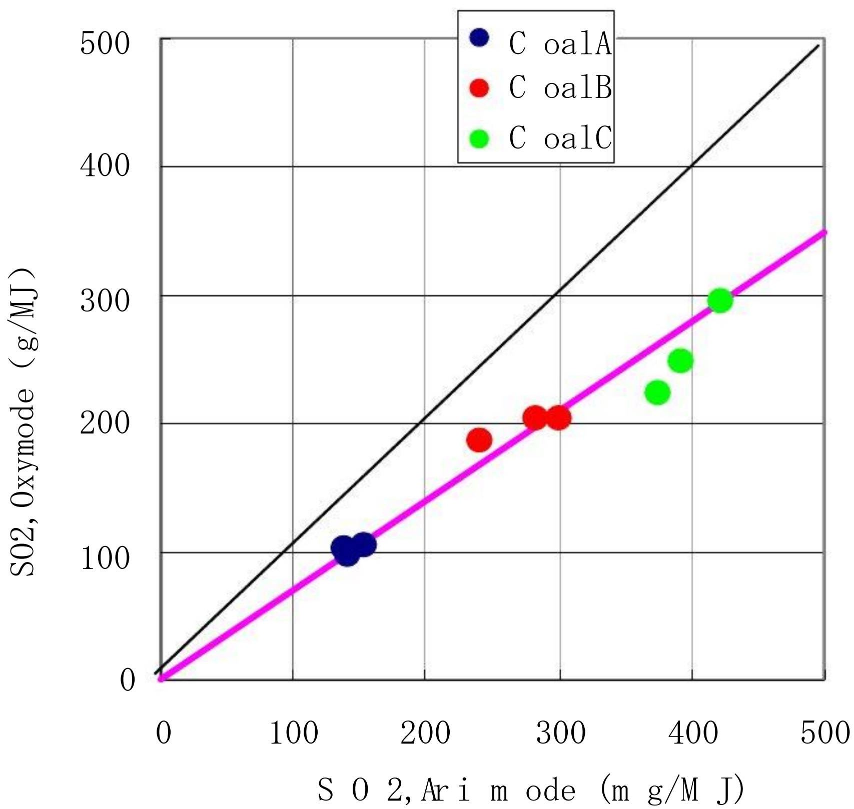
IHI – Callide Project Results (SO_2 Emissions)

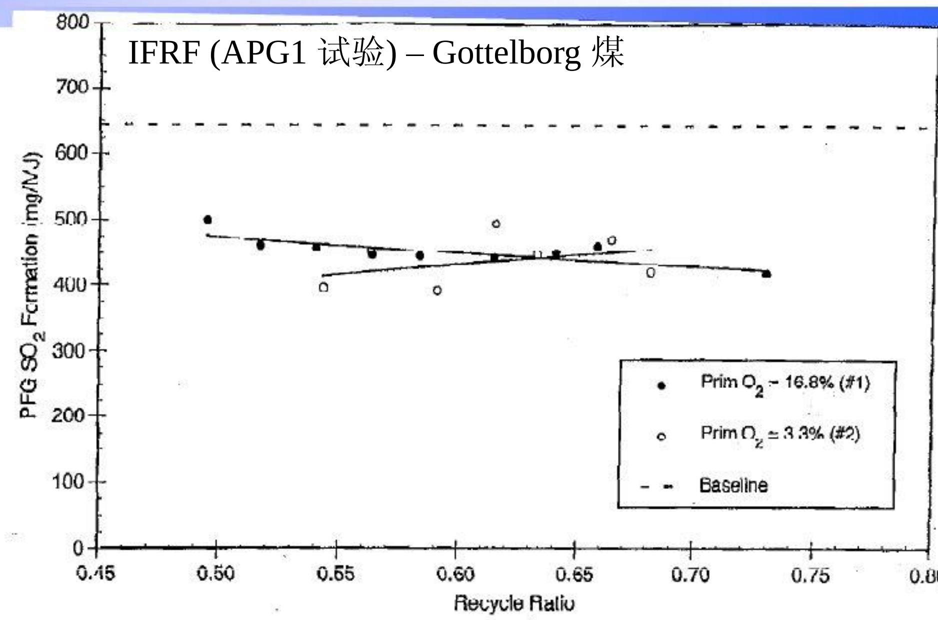


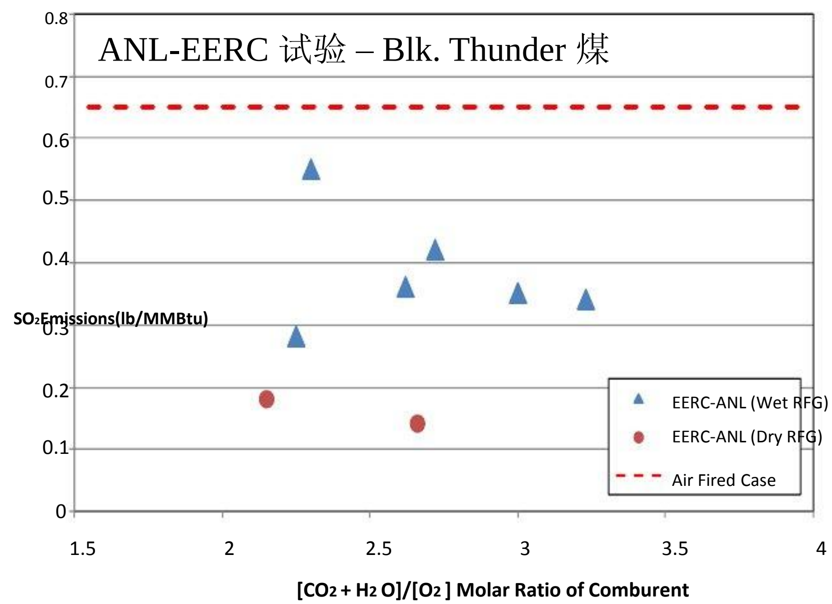




IHI – Callide项目结果(SO_2 排放)

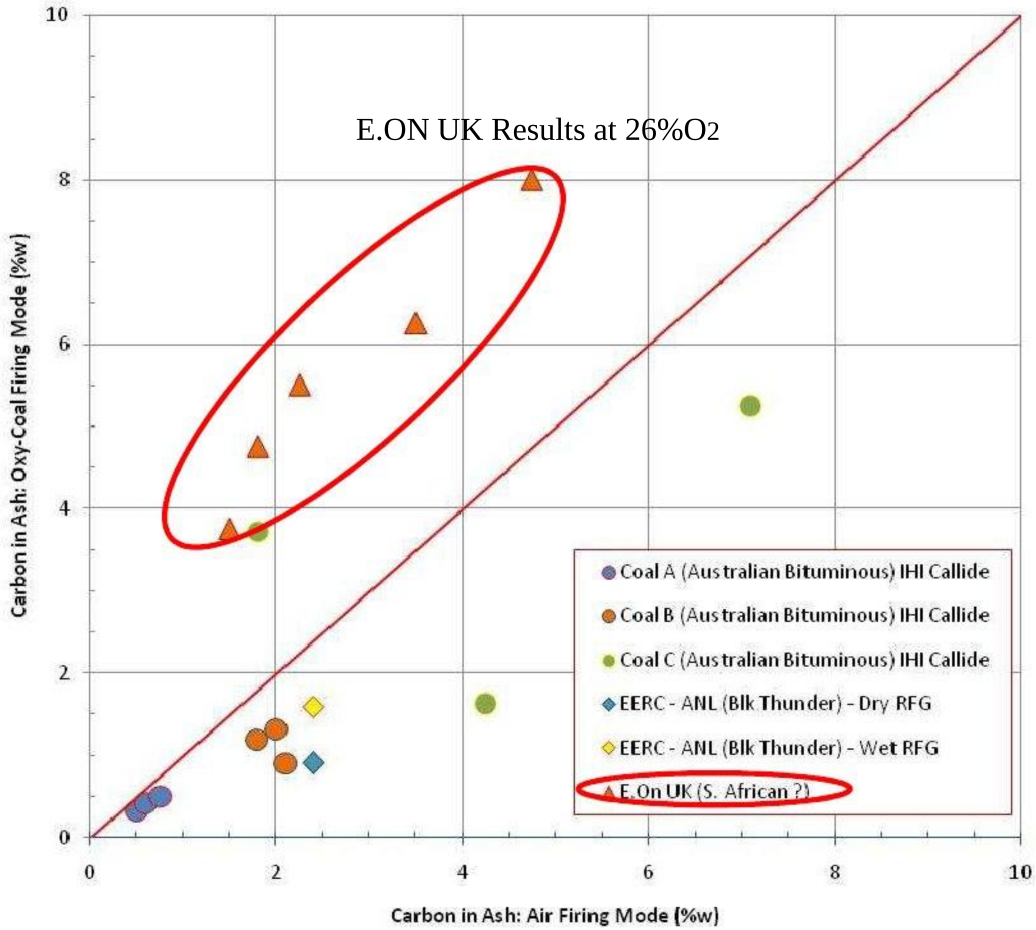


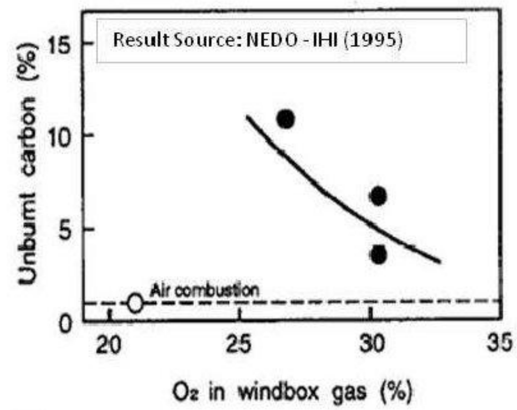


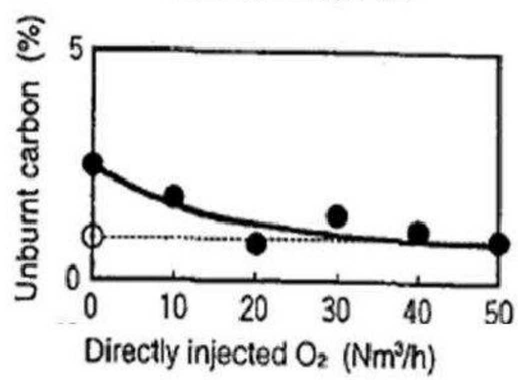


Would the capture of SO_2 / SO_3 in the ash enhanced by lower carbon in ash?

Marrier and Dibbs (1974) Thermochmica Act (Vol. 8)







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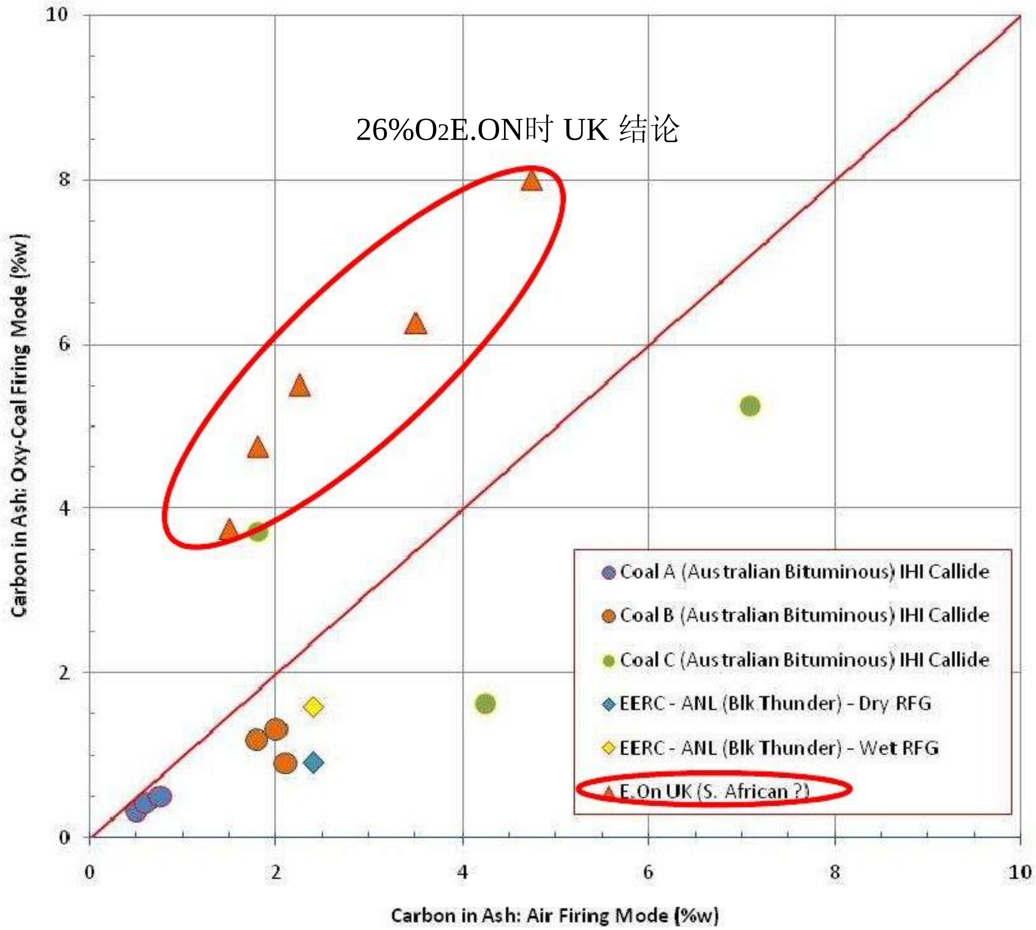
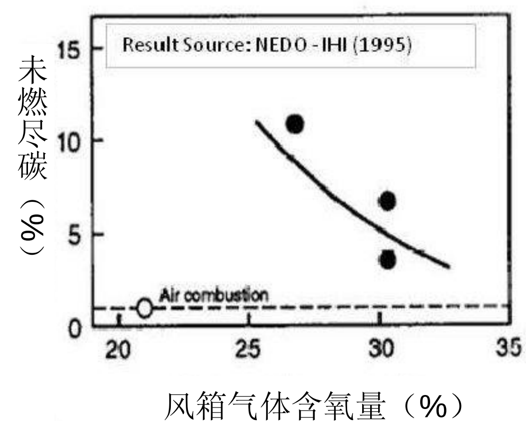
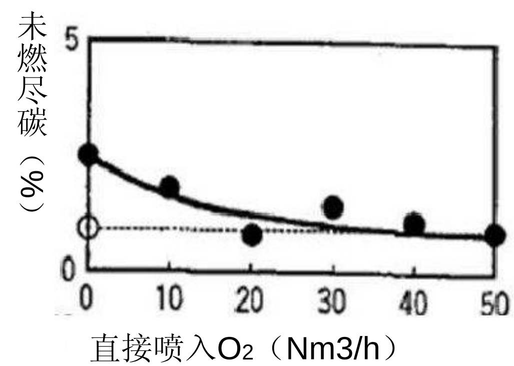
飞灰中含碳减少，SO_2 / SO_3 的捕集会增强吗?

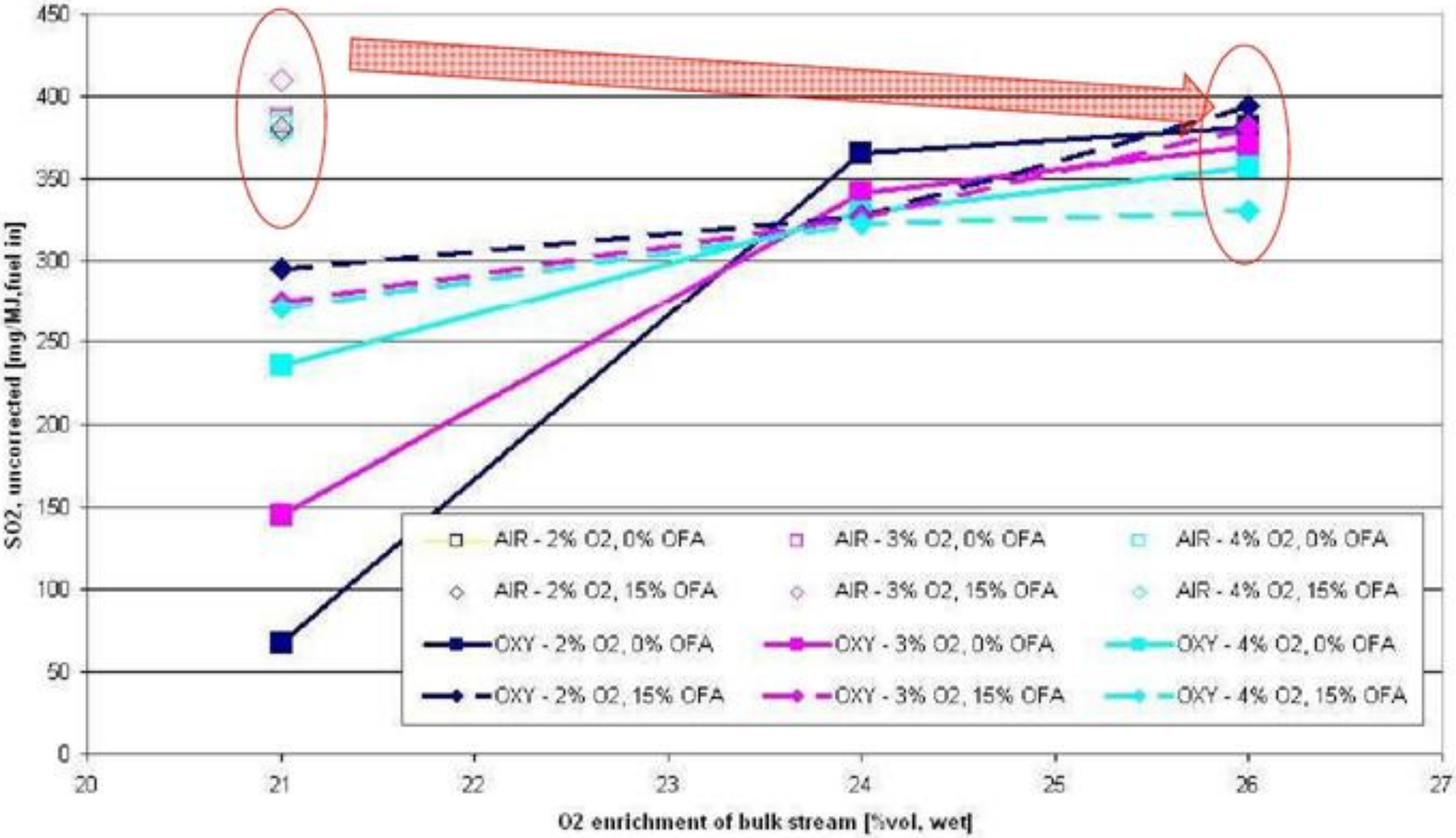
Marrier and Dibbs (1974) Thermochmica Act (Vol. 8)



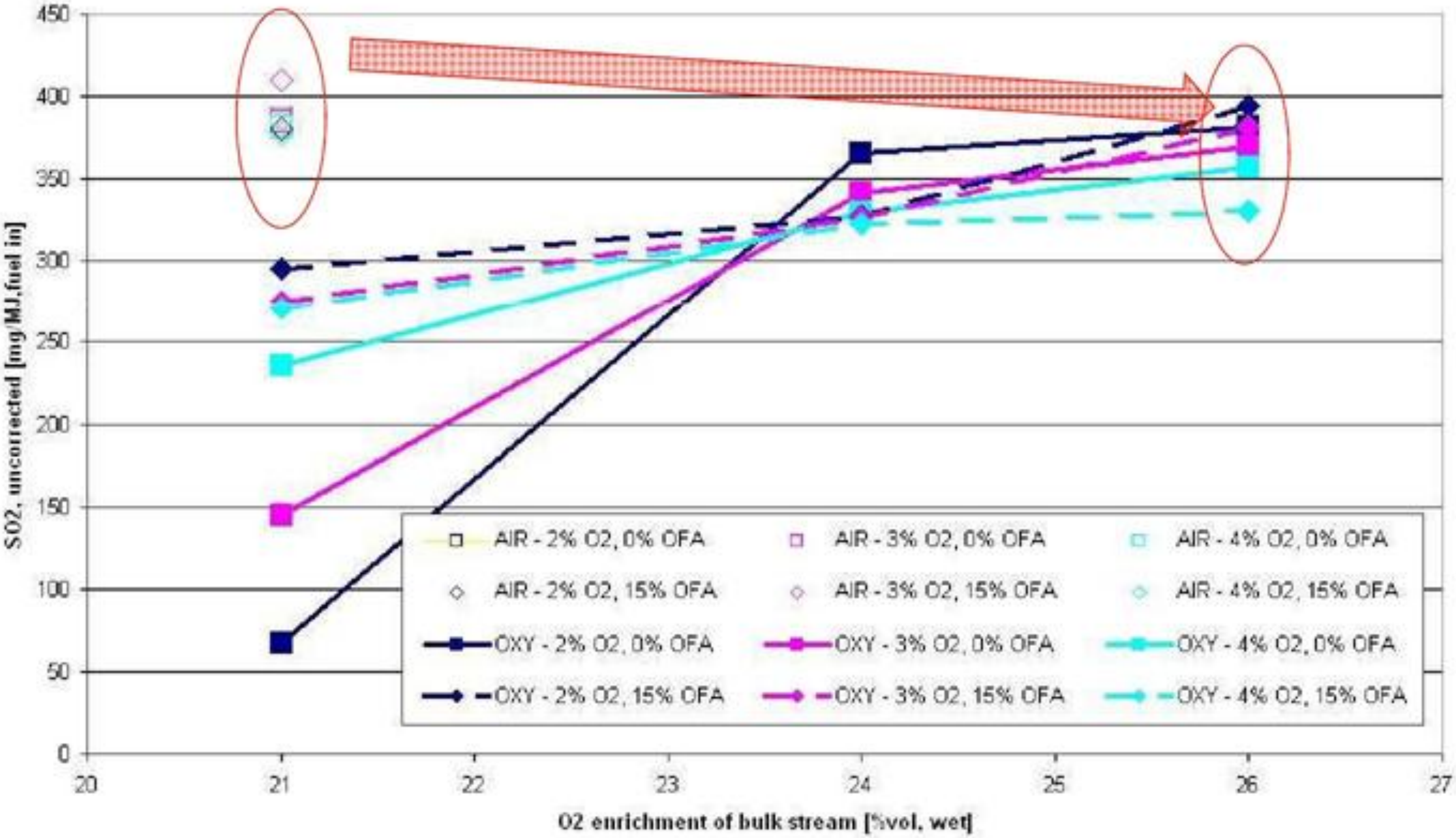




Emissions – SO_2

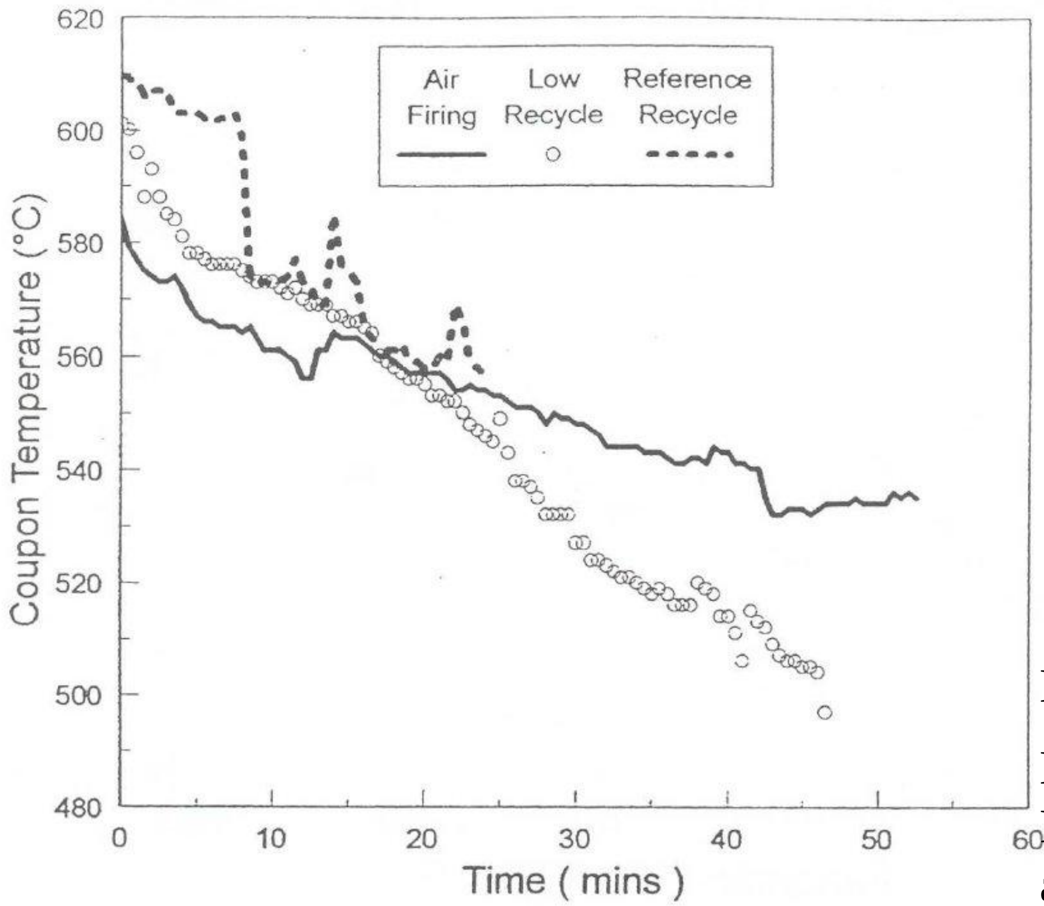


污染物排放 – SO_2



450
400
350
300
250
200
150
100
50
0
SO2, uncorrected [mg/MJ,fuel in]
20
21
22
23
24
25
26
27
O2 enrichment of bulk stream [%vol, wet]
AIR - 2% O2, 0% OFA
AIR - 3% O2, 0% OFA
AIR - 4% O2, 0% OFA
AIR - 2% O2, 15% OFA
AIR - 3% O2, 15% OFA
AIR - 4% O2, 15% OFA
OXY - 2% O2, 0% OFA
OXY - 3% O2, 0% OFA
OXY - 4% O2, 0% OFA
OXY - 2% O2, 15% OFA
OXY - 3% O2, 15% OFA
OXY - 4% O2, 15% OFA

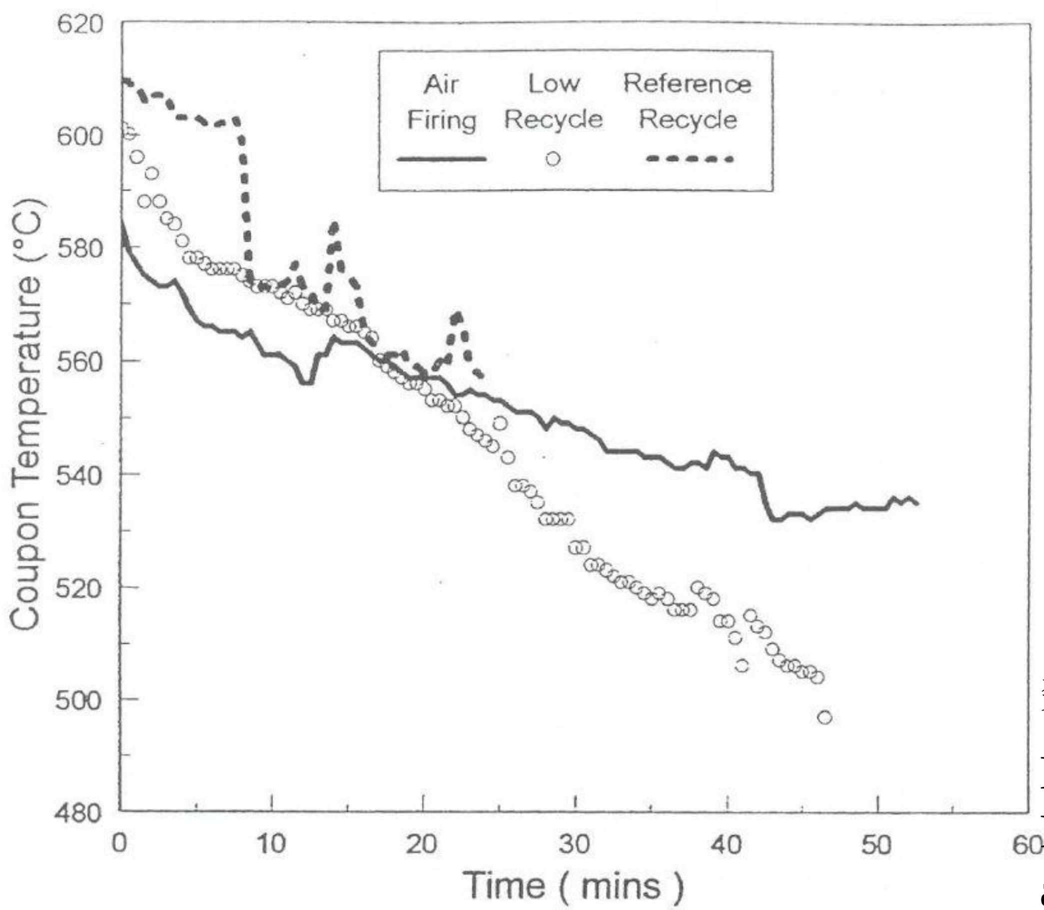
Ash Related Issue



Data from the trials taken by:

MBEL (Doosan Babcock), Air Products, Ulster University and Naples University (1995)

飞灰相关问题



数据来自以下单位的实验：

MBEL (Doosan Babcock), Air Products, Ulster University and Naples University (1995)

Summary SO_2/SO_3 and Sulphur in Ash – (1)

- ***Capture of sulphur in ash at the furnace section is primarily due to the high temperature direct sulphation mechanism as suggested by Okazaki et. al. (2001) as shown in their experimental results. This is pretty much in agreement to the in-flame SO_2 measurements done by IFRF during their APG2 trials.***
  - Okazaki et. al. suggested that this is due to promotion of capture of sulphur by CaO species and the inhibition of the decomposition of $CaSO_4$
  - This mechanism is further supported from the results of IVD Stuttgart (Maier et. al.) and Imperial College (Wrigley et. al.) indicating the occurrence of both carbonation and sulphation in the ash collected from oxy-coal combustion trials. This could indicate that equilibrium reactions promoting the formation of $CaCO_3$ and $CaSO_4$ are probably favoured (or highly enhanced) under CO_2 rich environment.
  - These results established the feasibility of using in-furnace SO_2 reduction by using $Ca(OH)_2$ or CaO injection.

飞灰中硫与SO_2/SO_3概述– (1)

- ***Okazaki等（2001）的实验结果表明，炉膛部分飞灰脱硫主要由于高温硫酸盐化。这与IFRF的APG2实验中SO_2的焰内测量结果高度一致。***

  - Okazaki等认为这与CaO 成分对脱硫的改善以及对$CaSO_4$分解的抑制有关。

  - IVD 斯图加特(Maier et. al.) 和帝国理工(Wrigley et. al.)的研究结果表明，富氧燃烧飞灰中同时存在碳酸盐化、硫酸盐化。这一结论进一步证明了上述机理。

    这也表明在富CO_2氛围中，促进$CaCO_3$和$CaSO_4$生成的平衡反应可能有优势。

  - 这些结论确定了喷入$Ca(OH)_2$ 或CaO实现炉内脱硫的可行性。

Summary SO_2/SO_3 and Sulphur in Ash – (2)

- ***Additional sulphur capture in ash could also be promoted by increased formation of SO_3.***
  - It should be recognised that both results from ANL-EERC and IVD Stuttgart confirms that SO_3 formation is higher (about 4-5 times – in terms of mass SO_3 emissions per unit energy input) as compared to air fired case. However, it is not yet clear if level of recycled SO_2 has it impact to the level of SO_3 formation.
  - Capture of sulphur by this mechanism would occur along the flue gas path (during the convective section) as shown in the results by IVD-Stuttgart.
    - Furthermore, IVD-Stuttgart results indicated that the higher the level of SO_2 are recycled , the capture efficiency of sulphur in ash is more efficient.
    - Nonetheless, it should be noted that that this observation in sulphur capture efficiency is coal dependent.

飞灰中硫与SO_2/SO_3概述– (2)

- ***SO_3的形成将增加飞灰对硫的捕捉***

  - ANL-EERC和IVD斯图加特的研究结果均证实，富氧燃烧比空燃产生的SO_3更多（约4~5倍——单位输入能量排放的SO_3质量）。但是，循环烟气中SO_2浓度是否对SO_3的形成有影响尚不清楚。

  - IVD斯图加特的研究结果表明，在流经的烟道（对流烟道）中存在上述机理的硫捕捉。

    - 同时，IVD斯图加特的研究结果还表明，SO_2的循环浓度越高，飞灰硫捕捉效率就越高。
    - 然而，必须注意的是这些关于硫捕捉效率的结论都与煤种有关。

Summary SO_2/SO_3 and Sulphur in Ash – (3)

- ***Results from Marrier and Dibbs (1974) further support the observations made by IVD Sttuttgart:***
  - maximum conversion of SO_2 to SO_3 would occur around 700-800^{o}C.
  - Capture of sulphur in ash could be dependent on the concentration of CaO and MgO in the ash. (This could probably be one of the reasons why capture efficiency of sulphur becomes coal dependent)
  - Iron oxides could enhanced the formation of SO_3 therefore promoting the capture of sulphur in the ash at the convective section. (This could probably be one of the reasons why capture efficiency of sulphur becomes coal dependent).
  - Carbon in ash could diminish the efficiency in the capture of sulphur in ash. This is supported by various studies indicating a lower carbon in ash during oxy-coal combustion trials (IHI, IFRF, ANL-EERC) showed a lower SO_2 emissions (i.e. higher degree of sulphur capture in ash). A higher carbon in ash by E.ON UK experimental results indicated a nearly similar SO_2 emissions to the air fired case.
- ***Higher ash deposition rate under the wet RFG trials could also promote higher sulphur capture in the convective section. This should be further validated!***

飞灰中硫与SO_2/SO_3概述 – (3)

- ***Marrier and Dibbs (1974)的研究结果进一步证实了TVD斯图加特的观点***
  - SO_2 到 SO_3 的最高转化温度在700-800℃范围内；
  - 硫的捕集依赖于飞灰中CaO 和MgO的含量（这也许是硫捕捉效率取决于煤种的原因之一）；
  - 氧化铁促进SO_3的形成，因此对流烟道硫的捕集得到加强（这也许是硫捕捉效率取决于煤种的原因之一）；
  - 飞灰含碳量会降低硫的捕集效率。 很多研究表明，煤的富氧燃烧试验(IHI, IFRF, ANL-EERC 中飞灰含碳量越低，SO_2排放越少，即硫的捕集效率越高。 E.ON UK实验结果表明，飞灰中高含碳量导致SO_2排放类似于空气燃烧。
- ***湿式RFG实验中，飞灰沉积速率越快，对流段硫的捕集效率越高。这还需进一步证实。***

Oxygen Production

CHALLENGES TO THE DESIGN AND ENGINEERING OF THE AIR SEPARATION UNIT

制氧

空分单元设计和工程的挑战

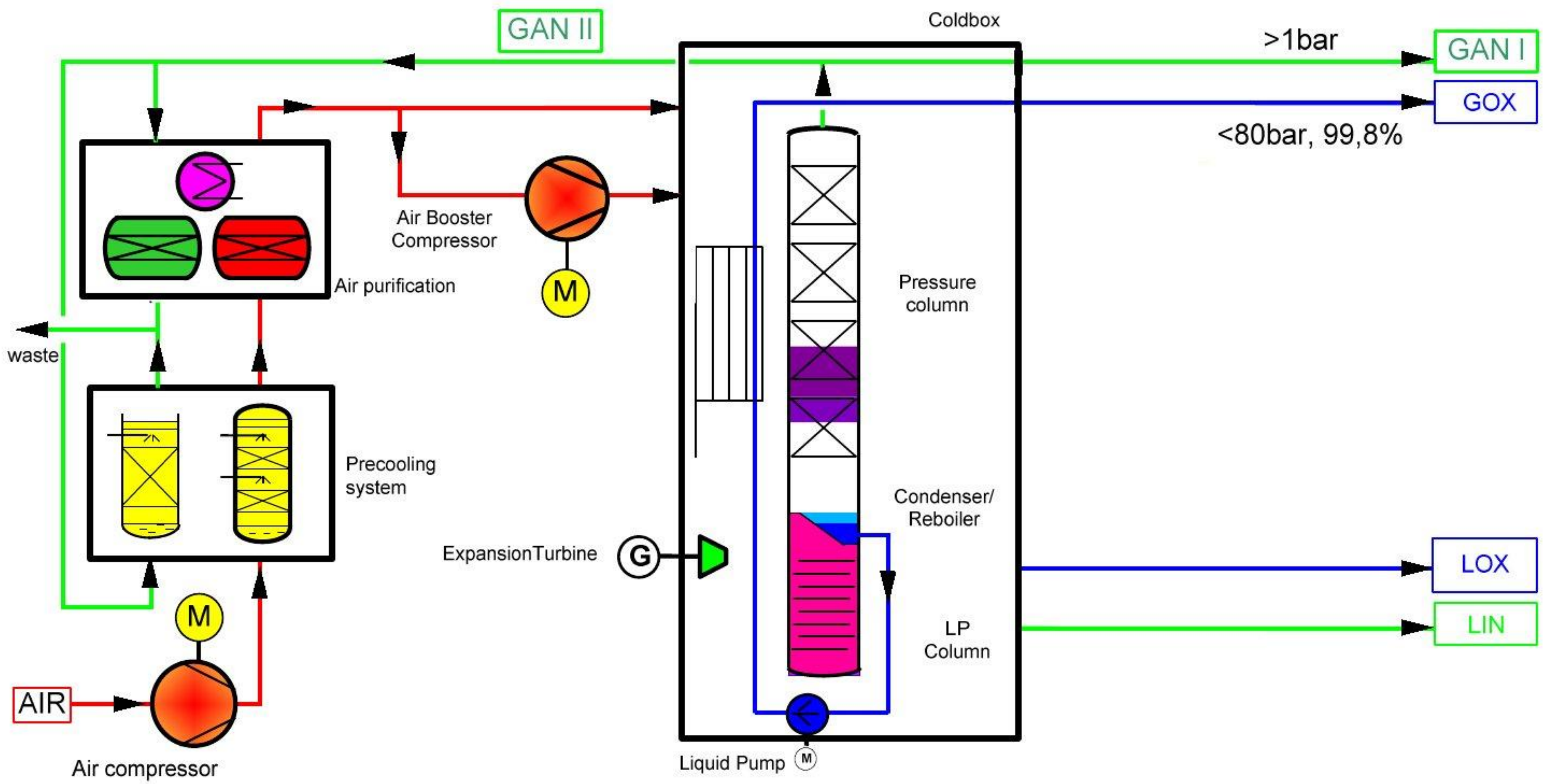
Challenges to Oxygen Production

- *As of today, the only available technology for oxygen production in large quantities is **cryogenic air separation.***
- *Advances and Development in ASU could result to 25% less energy consumption.*
  - These design would be based on either a 3 column design or dual reboiler design.
- *Challenges are:*
  - Cost of production of oxygen (energy consumption)
  - Utilisation of nitrogen within power plant.

制氧面临的挑战

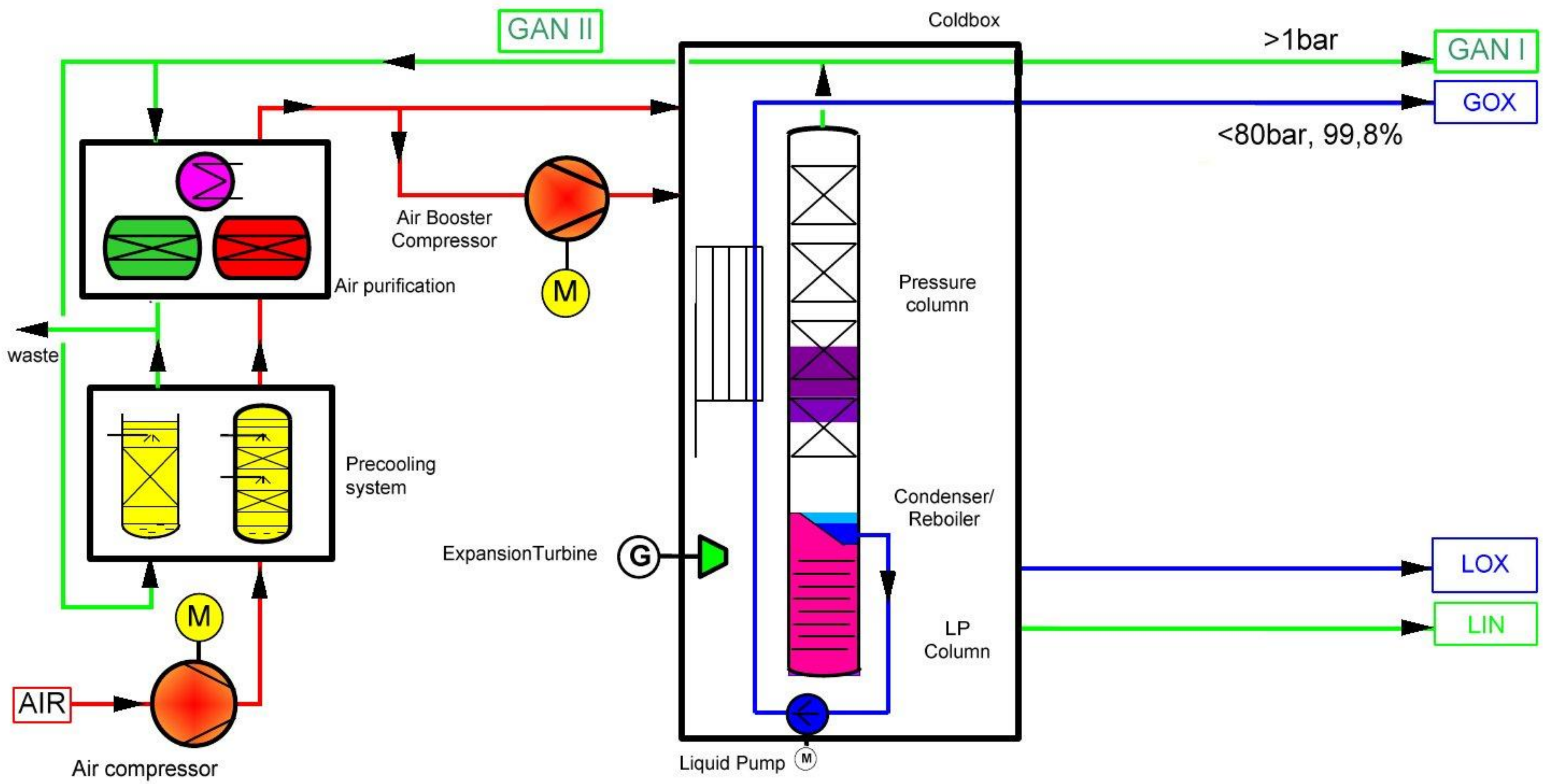
- *时至今日, 大规模制氧的唯一可行技术是低温空气分离*
- *ASU的改进将降低25%的能耗*
  - 基于三塔设计或双蒸发器设计
- *挑战如下:*
  - 制氧成本 （能耗）
  - 电厂中氮气的利用

Air Separation Plants
Simplified Air Separation Process



Air compression, -precooling and -purification	heat exchange, refrigeration, rectification and internal compression	product distribution

空分厂
简化的空分过程



空气压缩, 预冷和净化	换热, 制冷, 整流和内部压缩	产品 分布

Cryogenic Air Separation – Capacity Increase

1902 :
5 kg/h
(0,1 ton/day)

2006 :
1,250 Mio kg/h
(30.000 ton/day)

低温空气分离– 容量增加

1902 :
5 kg/h
(0,1 ton/day)

2006 :
1,250 Mio kg/h
(30.000 ton/day)

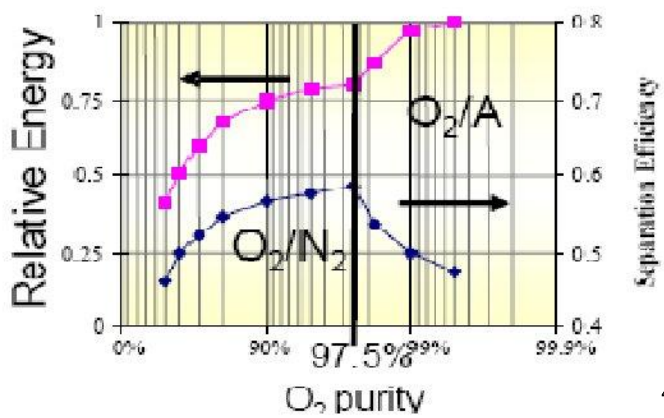
Air Separation Plants – Shell „Pearl“ GTL Project
Qatar
30.000 tons/day Oxygen

空分厂 – Shell „Pearl“ GTL 项目
Qatar
30.000 tons/day 氧气

Process Description: Oxygen Supply

- ***Optimum oxygen purity suggested:***
  - 95% - 97%
  - @ 95% O_2 you will have 2% N_2 and 3% Ar

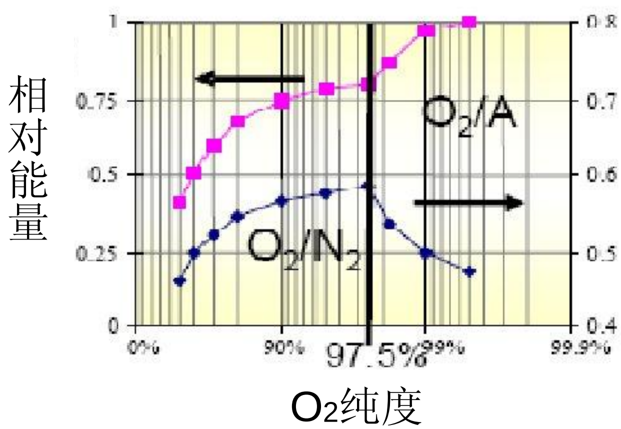
- ***higher purity not worthwhile due to:***
  - o Excess O_2 requirement (19%)
  - o Boiler air in leakage (1%)
  - o ESP air in leakage (2%)



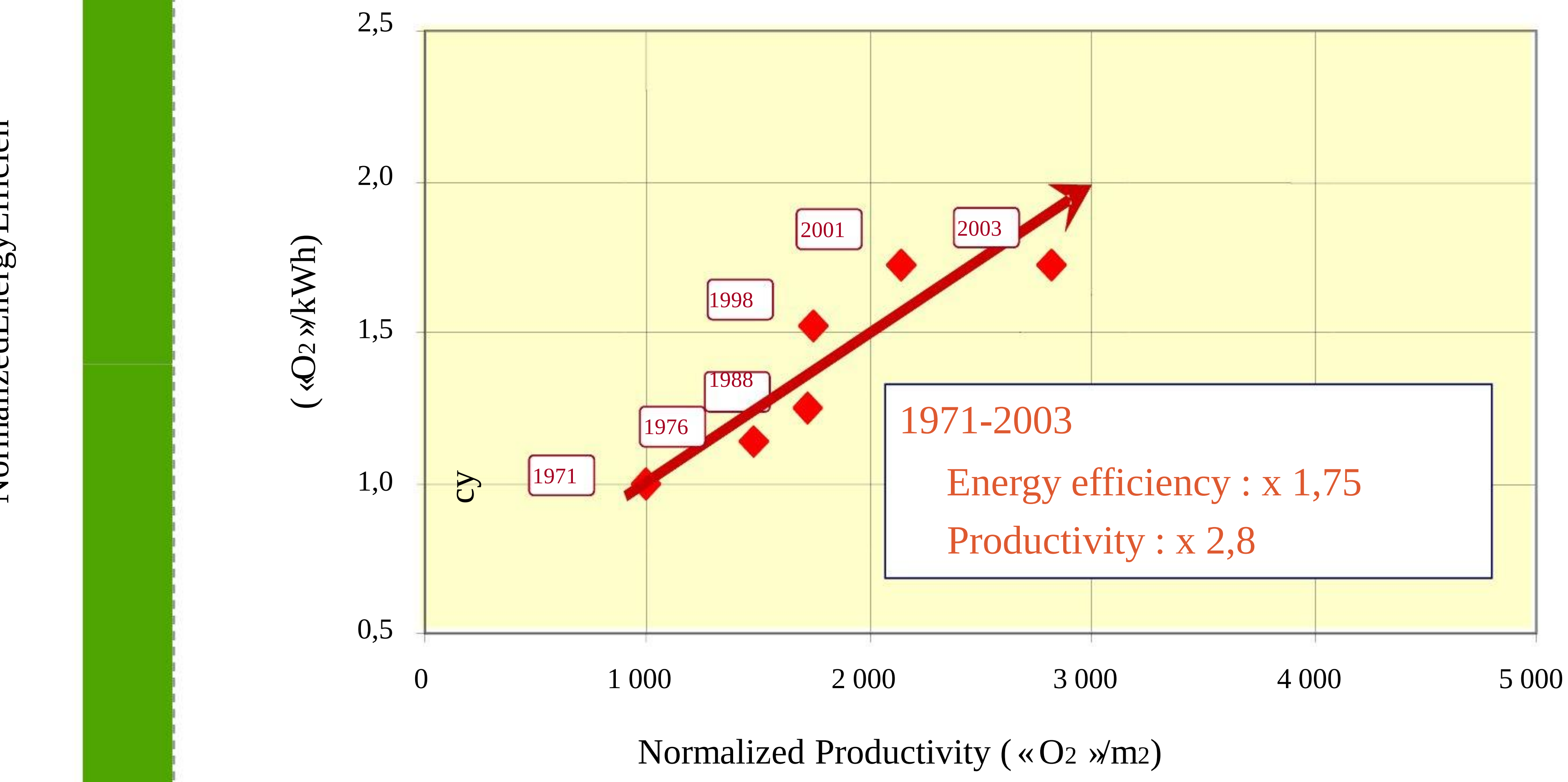
工艺描述: 供氧

- ***建议的最佳氧气纯度:***
  - 95% - 97%
  - 95% O_2 带有 2% N_2 和 3% Ar

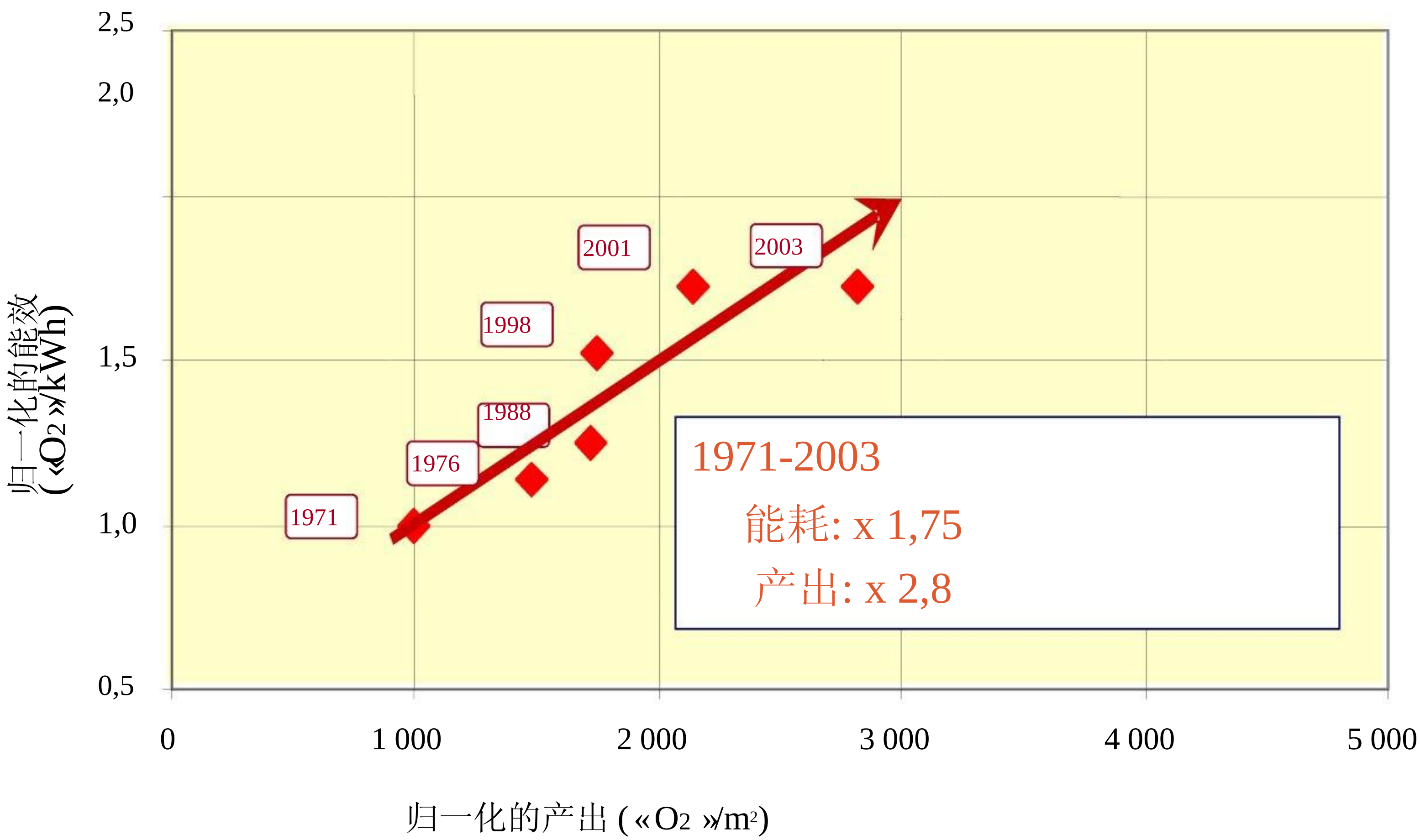
- ***无需更高纯度，因为:***
  - o 过量O_2要求(19%)
  - o 锅炉漏风 (1%)
  - o ESP 漏风 (2%)



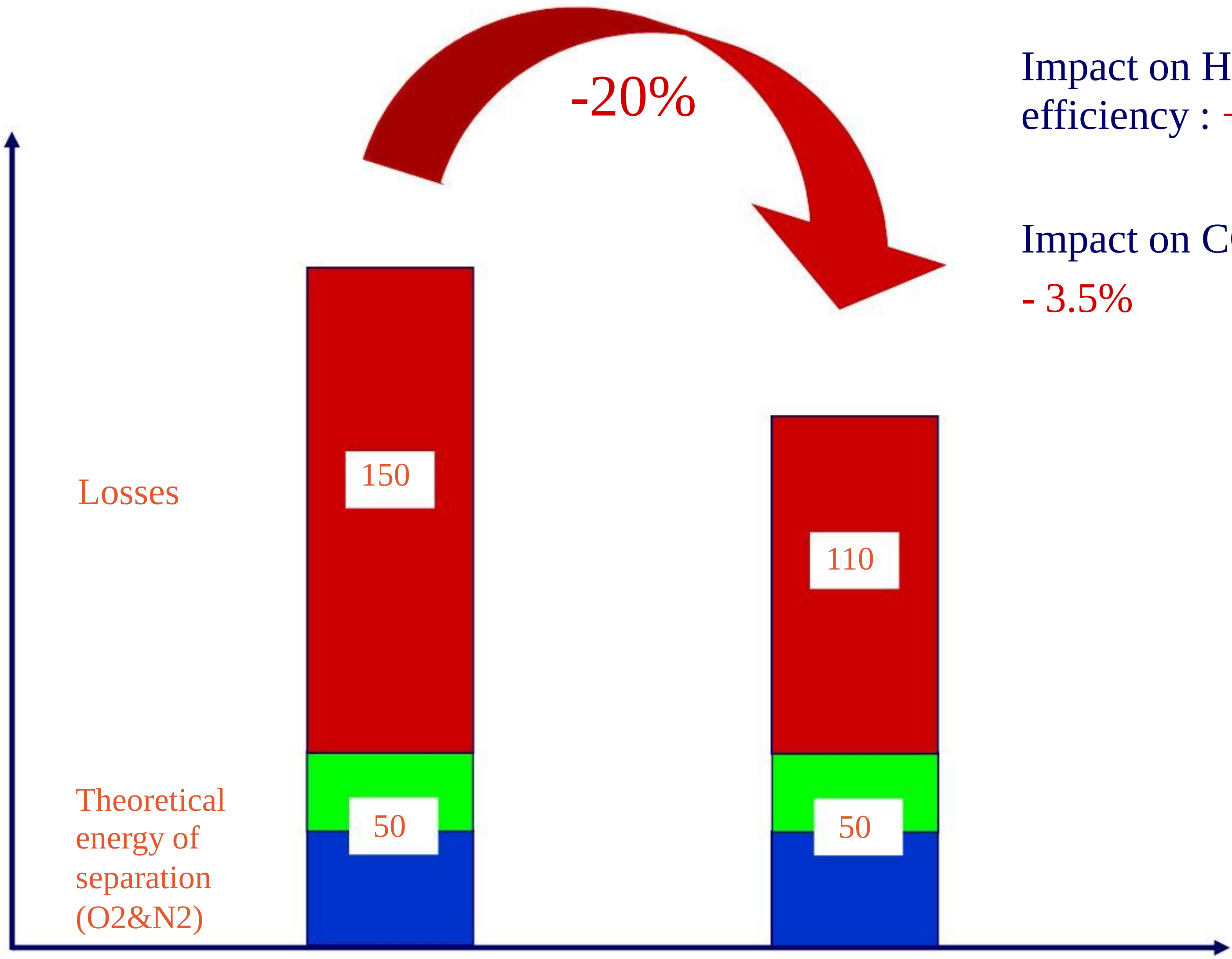
30 years of continuous Cryogenic ASU improvements



低温ASU三十年内的连续改进



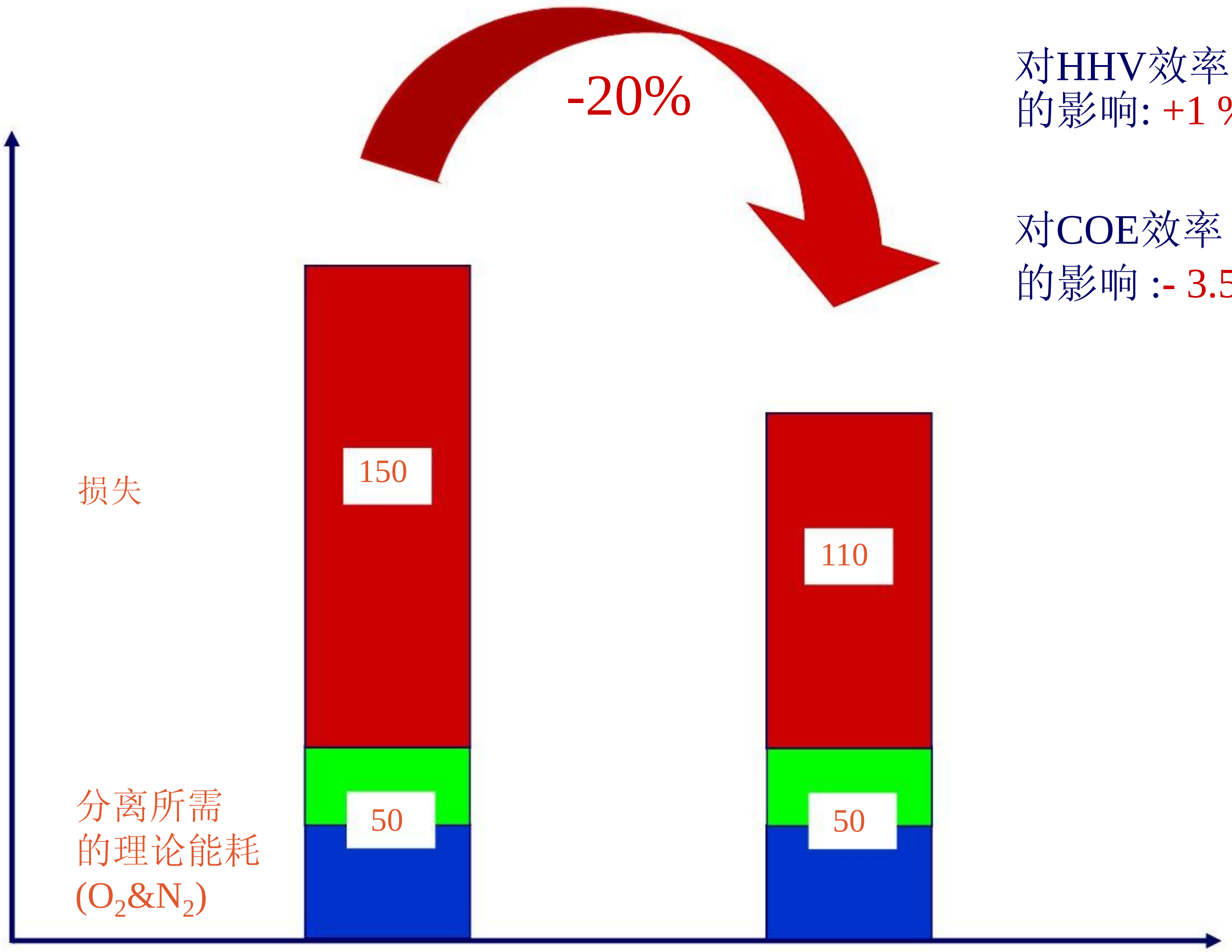
Specific energy of separation in kWh per ton of oxygen



Impact on HHV efficiency : +1 %

Impact on COE : - 3.5%

分离比能耗（ kWh/每吨氧气）

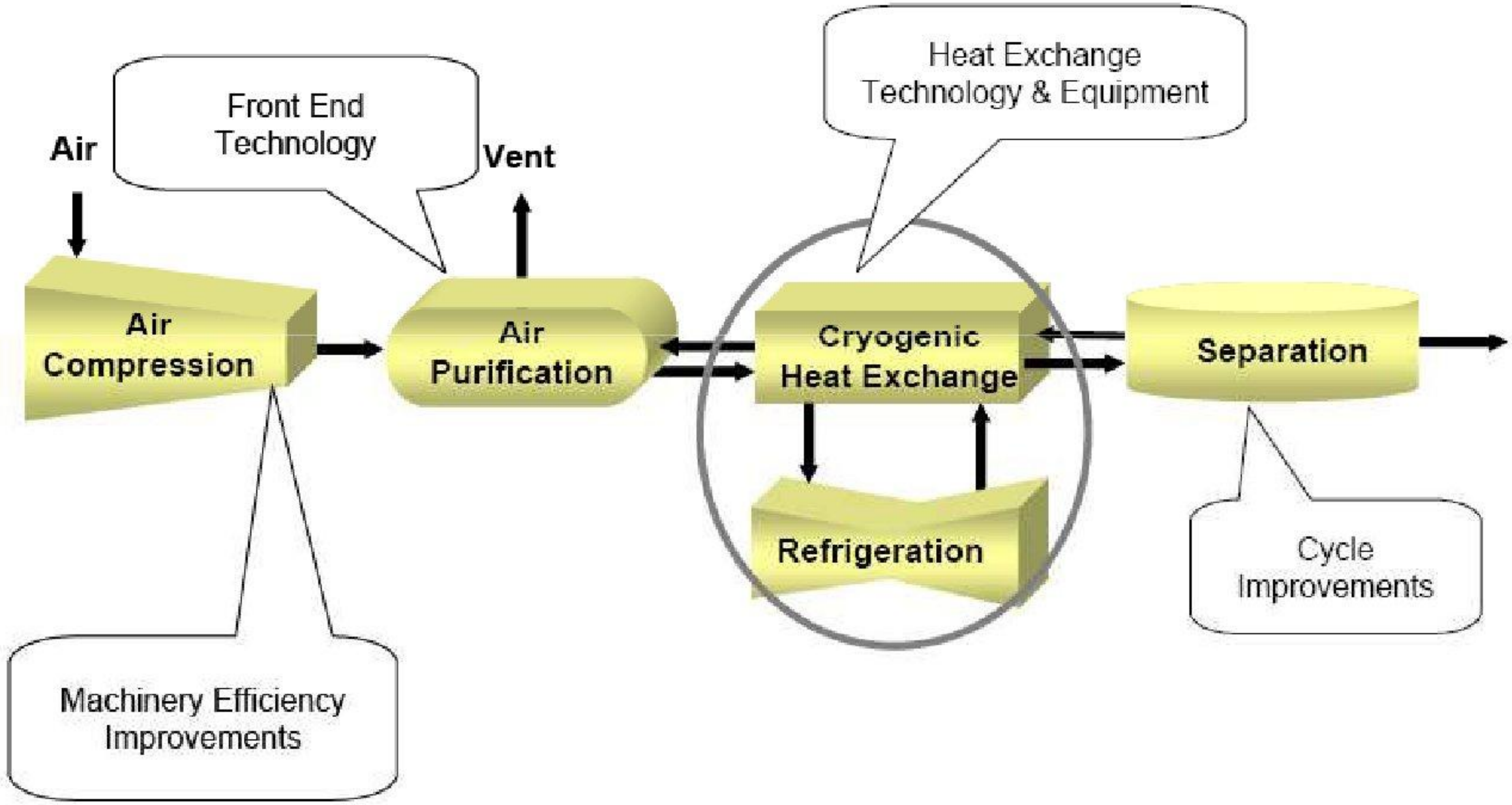


对HHV效率
的影响: +1 %

对COE效率
的影响 :- 3.5%

Power Consumption Reduction Opportunities

2012 Vision = 150-170 kWh/metric ton (*)

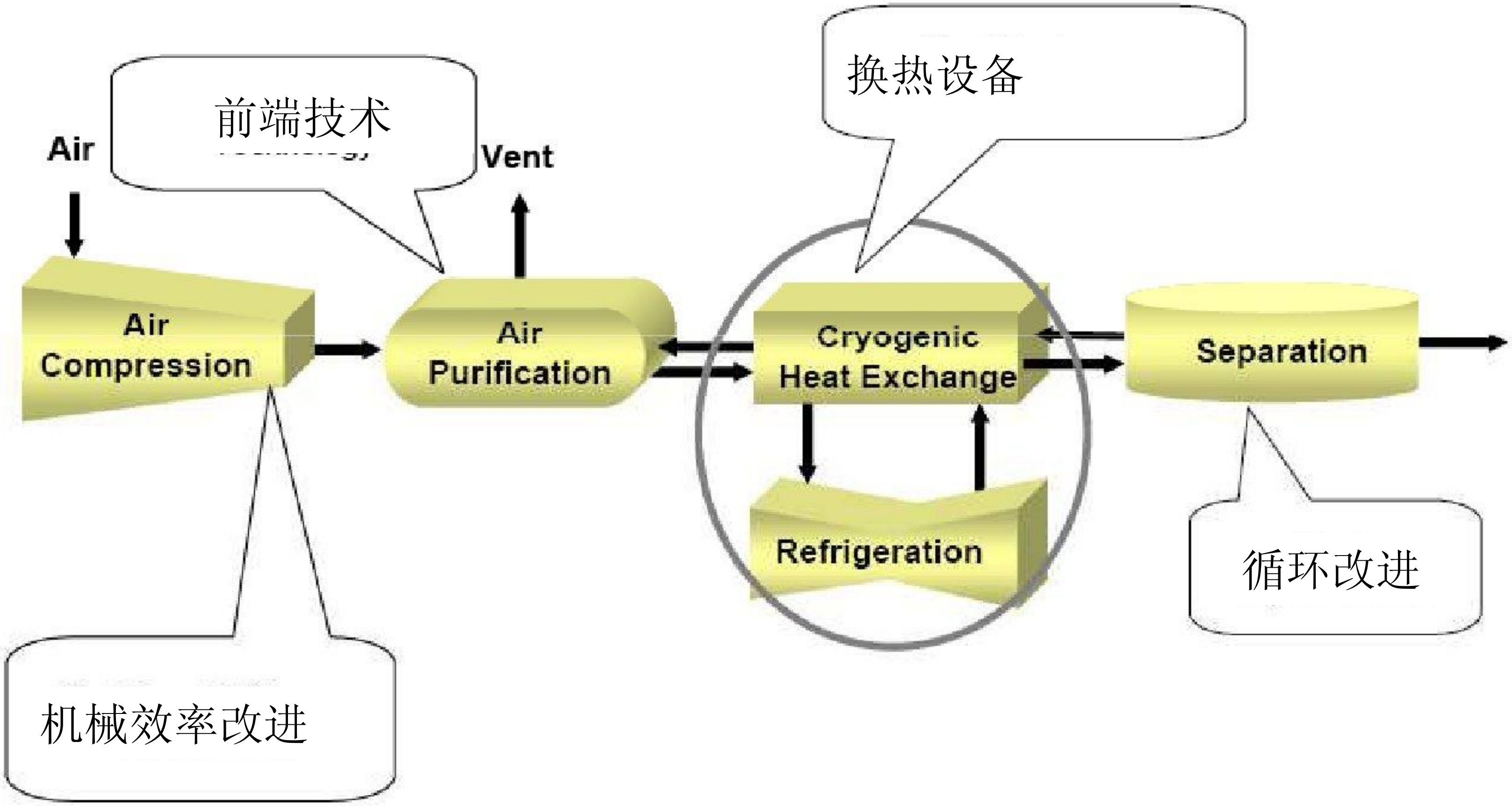


(*) 1 BAR – Gaseous Oxygen only - Depending of the relative valuation of capital and power costs

AIR PRODUCTS

降低能耗的机遇

2012展望=150~170kWh/公吨



(*) 1 BAR – Gaseous Oxygen only - Depending of the relative valuation of capital and power costs

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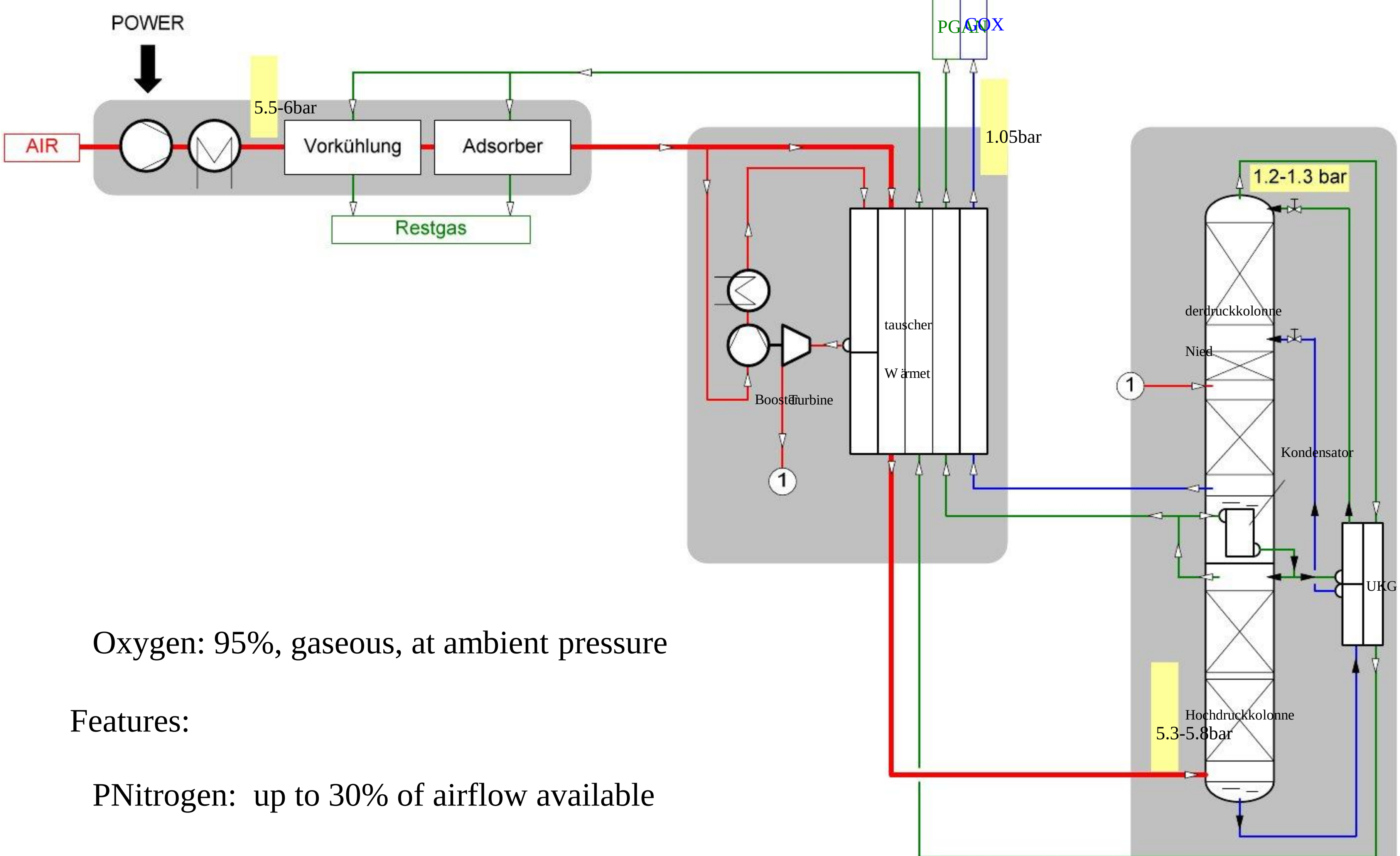
AIR PRODUCTS

Cryogenic Air Separation Process Optimization

低温空气分离工艺优化

Air Separation Process
Conventional Design (mit Einblaseturbine)

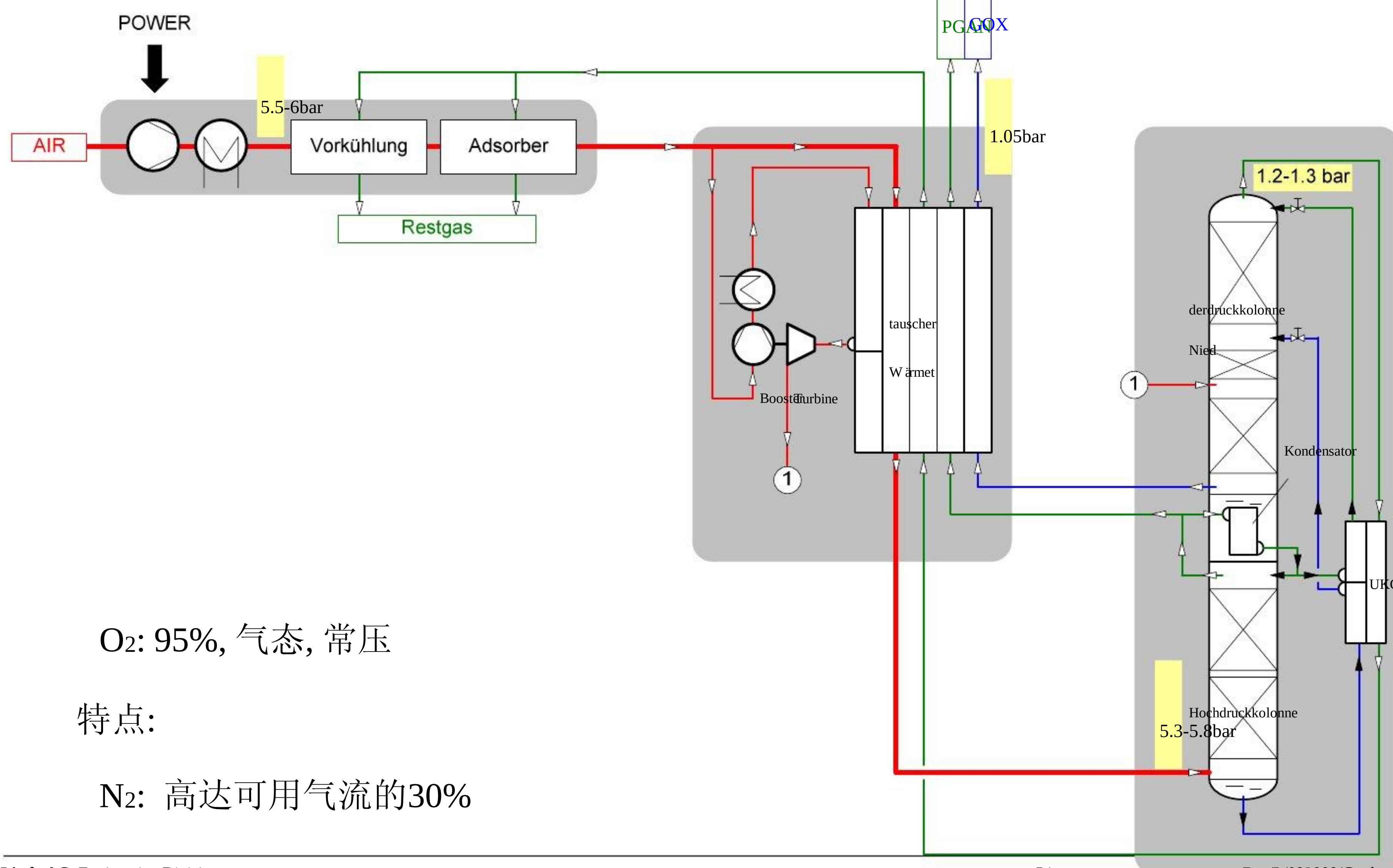


Oxygen: 95%, gaseous, at ambient pressure

Features:

PNitrogen: up to 30% of airflow available

空气分离工艺
常规设计(MIT Einblaseturbine)

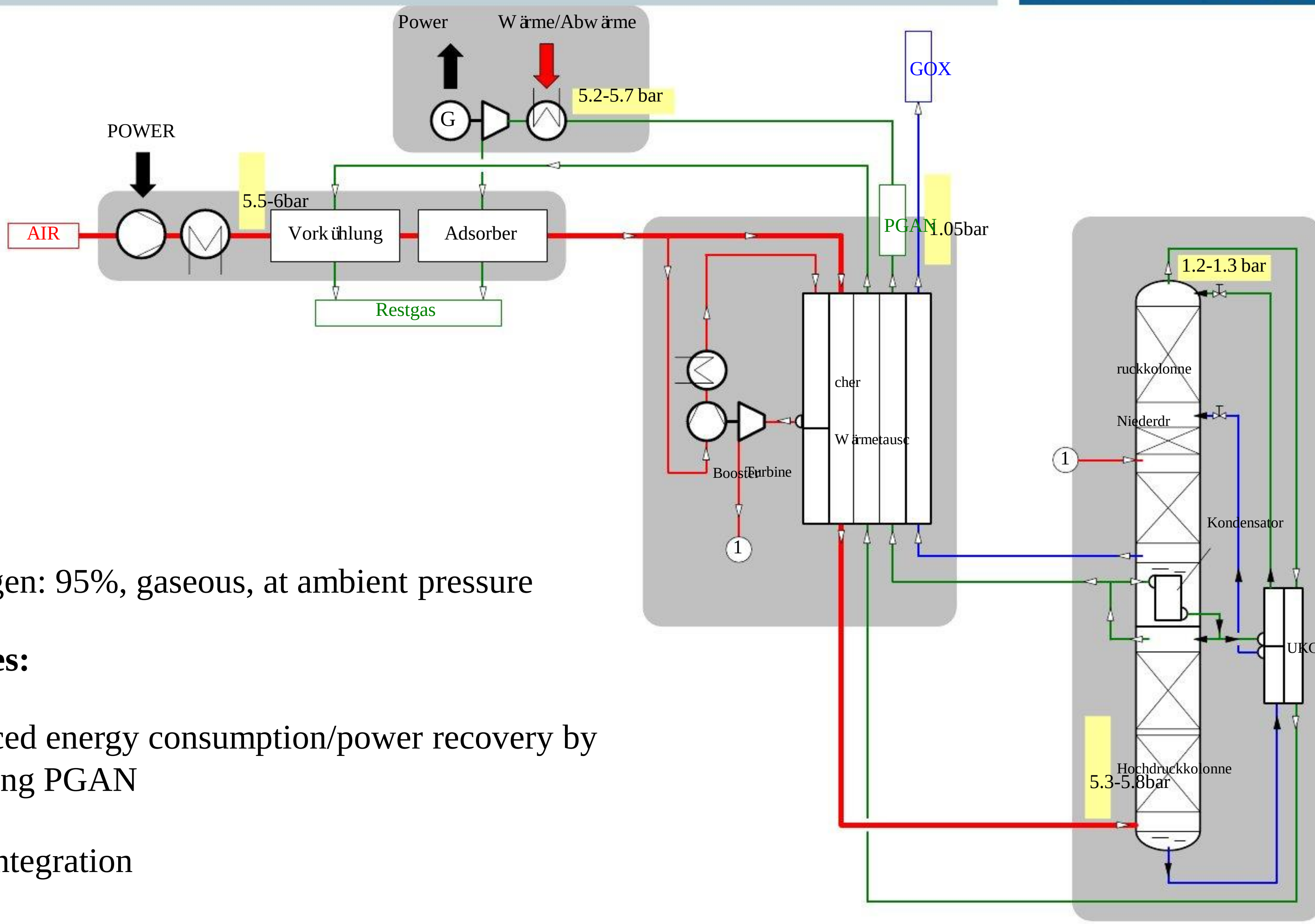


O_2: 95%, 气态, 常压

特点:

N_2: 高达可用气流的30%

Air Separation Process Advanced Alternative Design (mit warmer PGAN-Turbine)



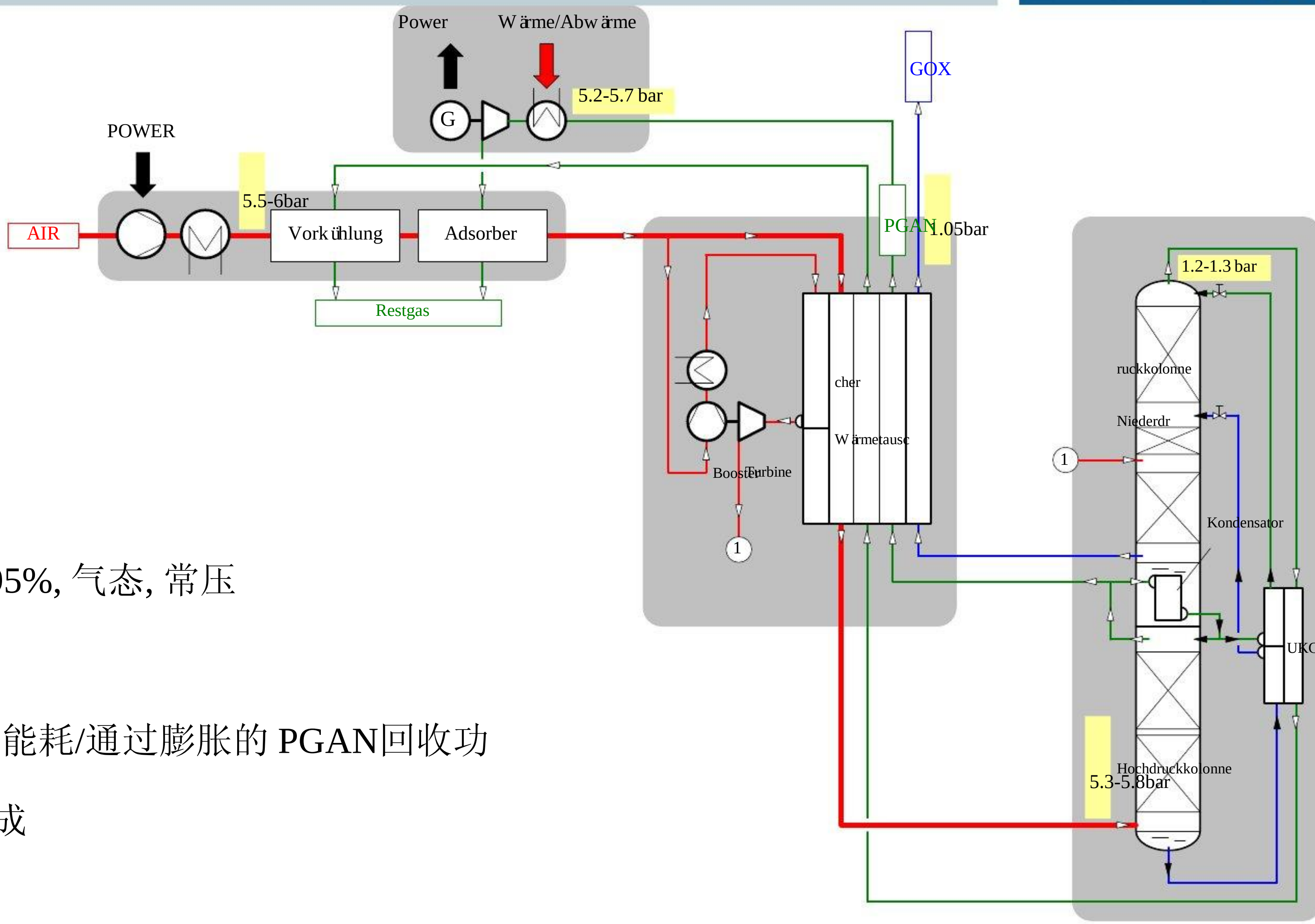
Oxygen: 95%, gaseous, at ambient pressure

Features:

reduced energy consumption/power recovery by expanding PGAN

heat integration

先进可替换的空分工艺设计
(mit warmer PGAN-Turbine)



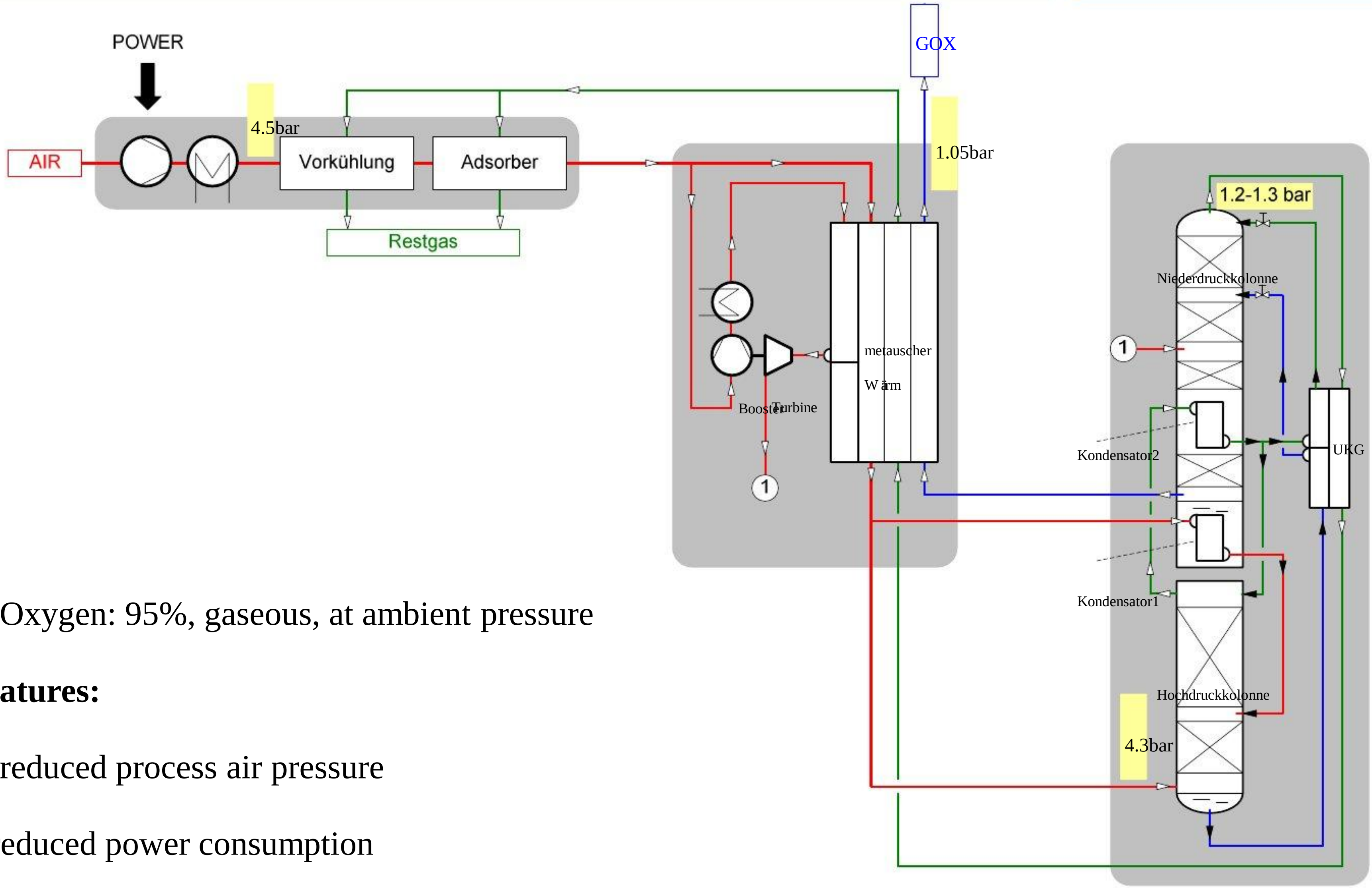
O2: 95%, 气态, 常压

特点:

减少能耗/通过膨胀的 PGAN回收功

热集成

Air Separation Process
Advanced Alternative Design ("Dual Reboiler"-Design)



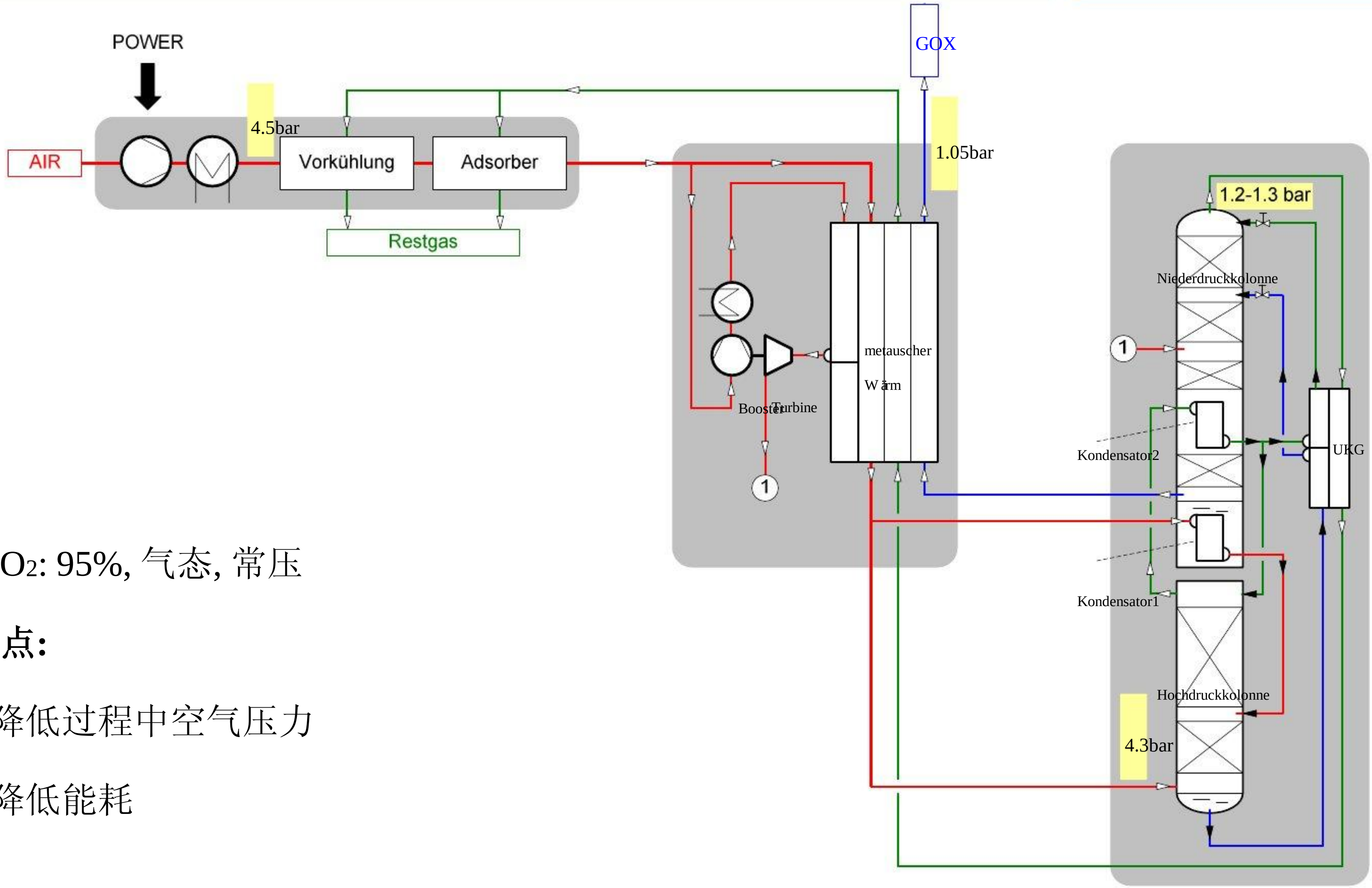
Oxygen: 95%, gaseous, at ambient pressure

Features:

reduced process air pressure

reduced power consumption

空分工艺
先进的替代设计(“双蒸发器” 设计)



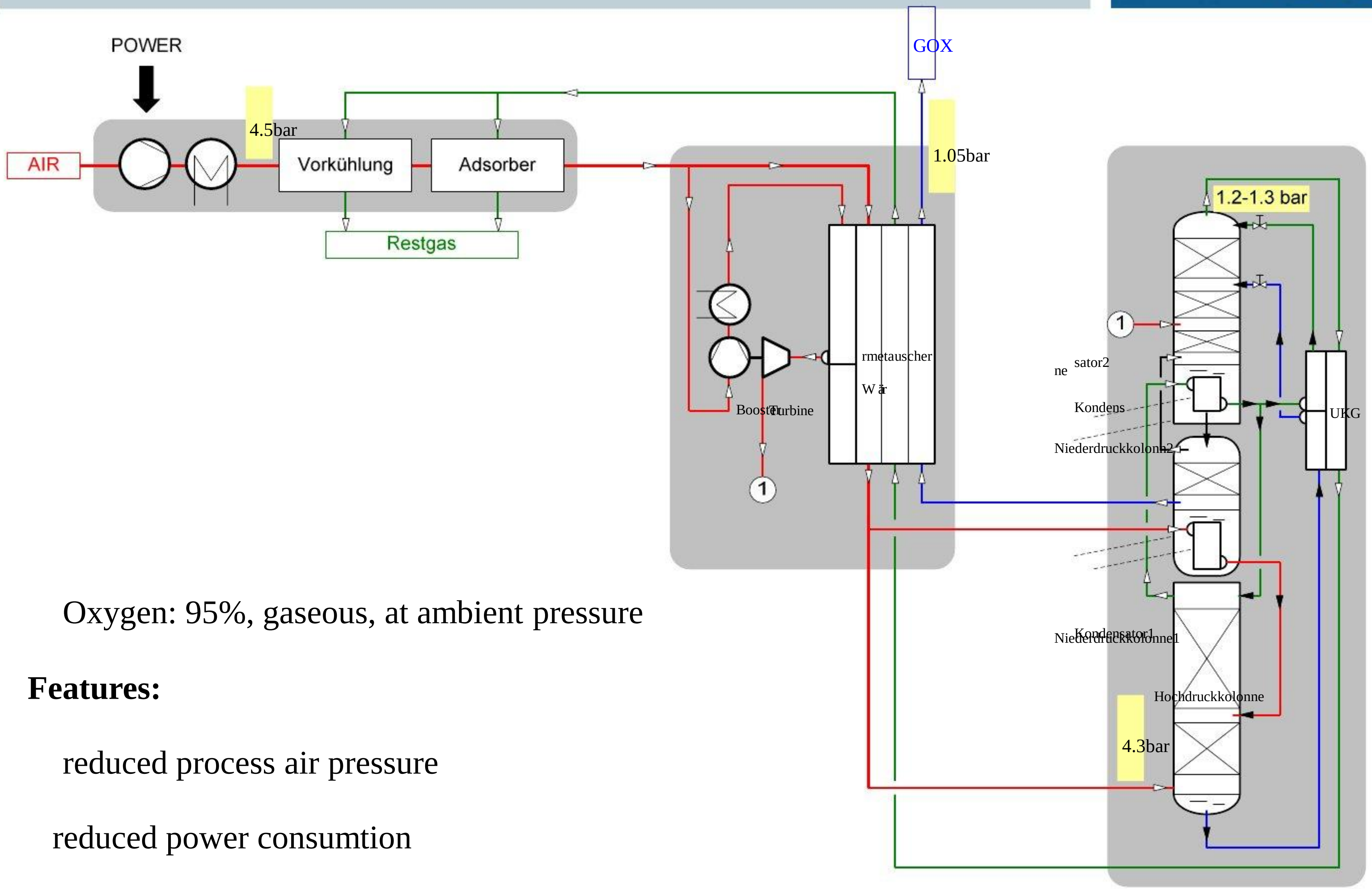
O2: 95%, 气态, 常压

特点:

降低过程中空气压力

降低能耗

Air Separation Process
Advanced Alternative Design (3-column Design)



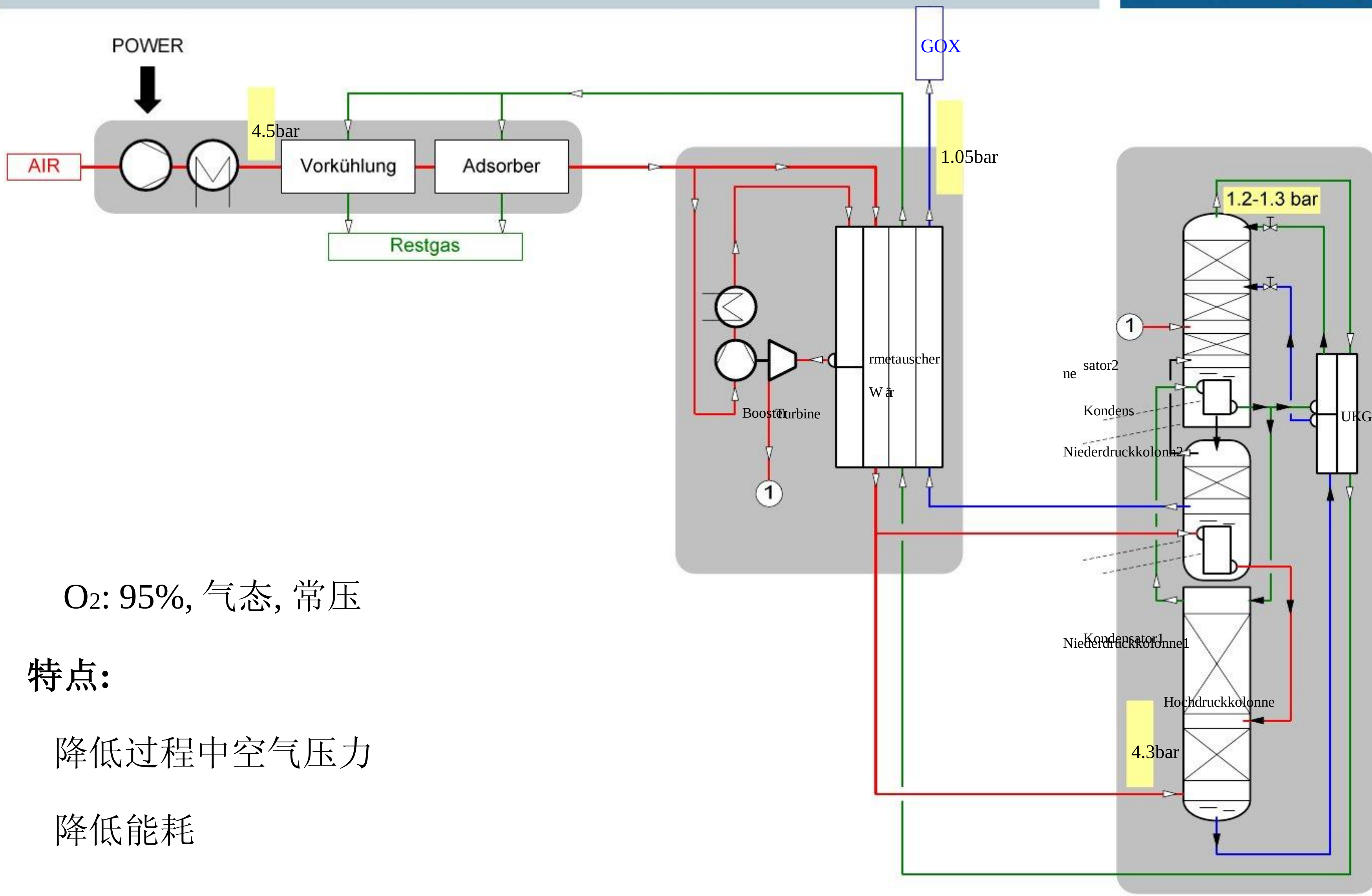
Oxygen: 95%, gaseous, at ambient pressure

Features:

reduced process air pressure

reduced power consumtion

空分工艺
先进的替代设计(三塔设计)



O_2: 95%, 气态, 常压

特点:

降低过程中空气压力

降低能耗

What are the remaining issues…

- ***~10,000 TPD of O_2 is required for a 500MWe (net) oxy-coal power plant with CCS.***
  - This means that you will need 2 single trains of 5000 TPD ASU
- ***Remaining Issues***
  - What could be the maximum capacity of oxygen production per train?
  - Operation flexibility (i.e. load following, etc…)
  - What will you do about the large volume of Nitrogen produced from this ASU?

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还存在哪些问题……

- ***带有CCS的500MWe（净）富氧燃烧煤粉电站，需要约10000t/d 氧气***
  - 这意味着需要两套5000t/d ASU

- ***存在的问题***
  - 每套ASU最大制氧能力
  - 运行的灵活性 （如负荷跟随等）
  - 产生的大量N_2该如何处理？

Where are the other gaps in R&D for oxygen production?

- ***Non-conventional oxygen production***
  - ITM – ions transport membrane (Air Products)
  - OTM – oxygen transport membrane (Praxair)
  - CAR – ceramics autothermal recovery (Linde / BOC)

- ***Chemical Looping Combustion***

制氧研发中可能的突破口

- *非常规的制氧工艺*
  - ITM – 离子输送膜(Air Products)
  - OTM – 氧输送膜(Praxair)
  - CAR –变压吸附自热回收陶瓷(Linde /BOC)

- *化学链燃烧*

CO_2 Processing Unit

WHAT ARE THE KEY ISSUES IN DETERMINING THE DESIGN PRINCIPLES OF A CO2 PROCESSING UNIT

CO_2 处理单元

CO2处理单元设计原理的关键因素是什么

Challenges to CO_2 Processing Unit

- ***The CO_2 processing unit could be very competitive business (an important growth area) for industrial gas companies.***

- ***Challenges are:***
  - Demand of the quality requirements of the CO_2 from the power plant for transport and storage. **What are the Required Specification?**
  - Further recovery of CO_2 from the vent will make oxyfuel more competitive if high recovery of CO_2 is required!
  - Further recovery of energy through integration with ASU or boiler would provide further energy savings.
  - **Need a large scale demonstration of the CO_2 processing unit using impure CO_2 as refrigerant.**

CO_2 处理单元的挑战

- **CO_2 处理单元对工业气体公司可能成为一项非常有竞争力的业务 (非常重要的增长点)**

- **面临的挑战是:**
  - 运输和储存过程中对于电厂CO_2的质量要求

    具体的要求？
  - 如果要求高的CO_2 回收率，出口CO_2的进一步回收将使得富氧燃烧技术更有竞争力
  - 通过联合ASU或锅炉回收能量将会进一步节能。
  - **需要大型CO_2处理单元示范装置，能够处理不纯的 CO_2**

Purification of Oxyfuel-Derived CO2 for Sequestration or EOR

- ***CO_2 produced from oxyfuel requires purification***
  - Cooling to remove water
  - Inert removal
  - Compression
- ***Current design has limitations***
  - SOx/NOx removal
  - Oxygen removal
  - Recovery limited by phase separation
- ***Necessary to define CO_2 quality requirement!!!***

用于埋存或EOR 的富氧燃烧产生的CO_2纯度

- ***富氧燃烧所得CO_2需要净化***
  - 冷凝除水
  - 脱除其他成分
  - 压缩
- ***现有设计的缺陷***
  - 脱除SOx/NOx
  - 除O_2
  - CO_2回收受到相分离的限制
- ***有必要定义CO_2的质量要求!!!***

Air Product's
"Sour Compression Process"

Air Product的
“酸性压缩工艺”

NOx SO_2 Reactions in the CO_2 Compression System

We realised that SO_2, NOx and Hg can be removed in the CO_2 compression process, in the presence of water and oxygen.

SO_2 is converted to Sulphuric Acid, NO_2 converted to Nitric Acid:

– $NO + \frac{1}{2} O_2$	=	NO_2	(1) Slow
– $2\ NO_2$	=	N_2O_4	(2) Fast
– $2\ NO_2 + H_2O$	=	$HNO_2 + HNO_3$	(3) Slow
– $3\ HNO_2$	=	$HNO_3 + 2\ NO + H_2O$	(4) Fast
– $NO_2 + SO_2$	=	$NO + SO_3$	(5) Fast
– $SO_3 + H_2O$	=	H_2SO_4	(6) Fast

Rate increases with Pressure to the 3rd power

- **only feasible at elevated pressure**

No Nitric Acid is formed until all the SO_2 is converted

Pressure, reactor design and residence times, are important.

CO_2压缩系统中NO_x、SO_2的反应

在有水和氧气存在的环境下，**SO_2、NO_x 和Hg**能够在 **CO_2** 压缩过程中脱除。

SO_2 转化成硫酸, NO_2 转化成硝酸:

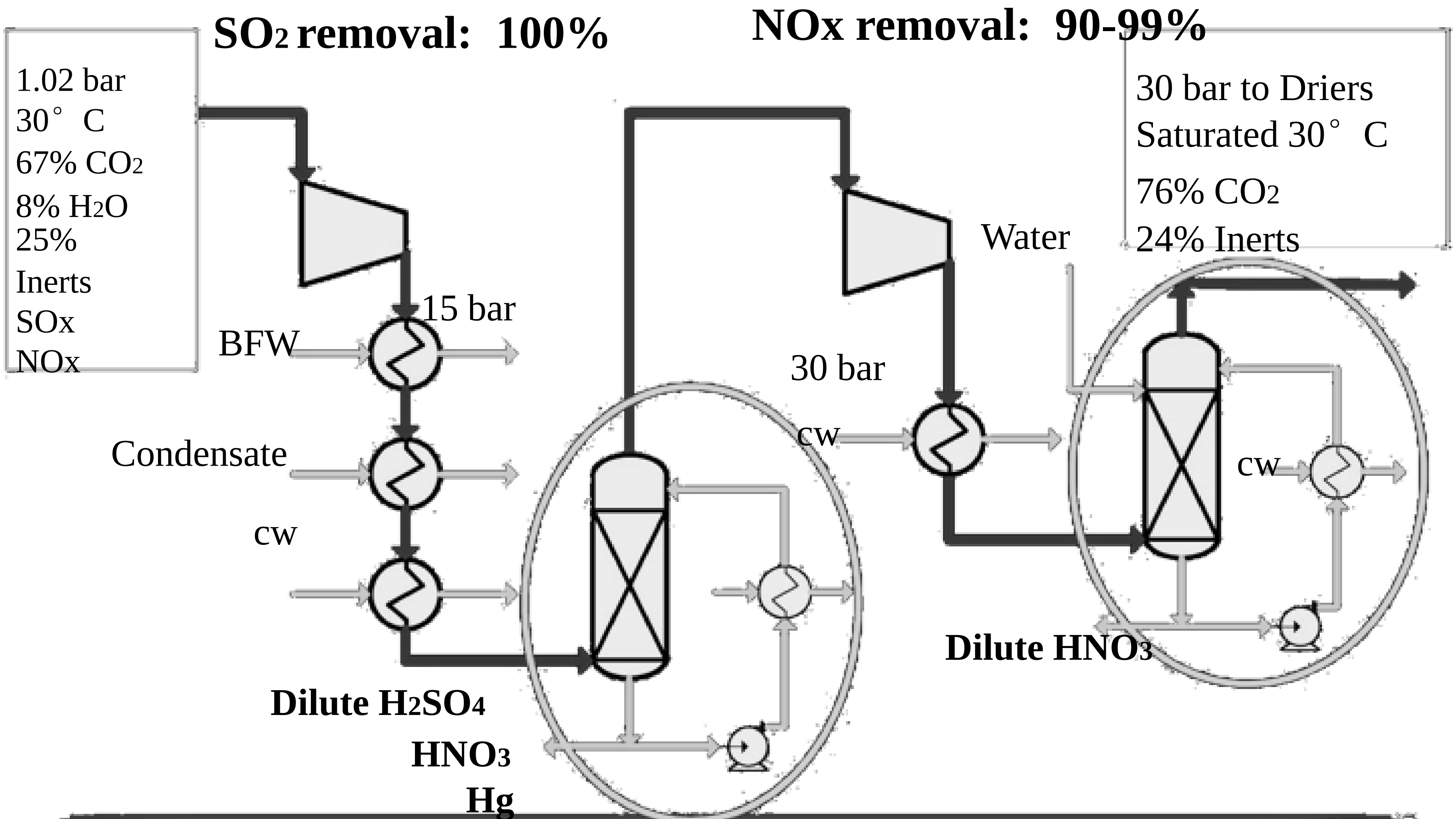
- $NO + \frac{1}{2} O_2 = NO_2$ (1) 慢
- $2 NO_2 = N_2O_4$ (2) 快
- $2 NO_2 + H_2O = HNO_2 + HNO_3$ (3) 慢
- $3 HNO_2 = HNO_3 + 2 NO + H_2O$ (4) 快
- $NO_2 + SO_2 = NO + SO_3$ (5) 快
- $SO_3 + H_2O = H_2SO_4$ (6) 快

反应速率随着压强的升高而增加——只有在高压下才可行

只有SO_2完全转化了才会生成硝酸

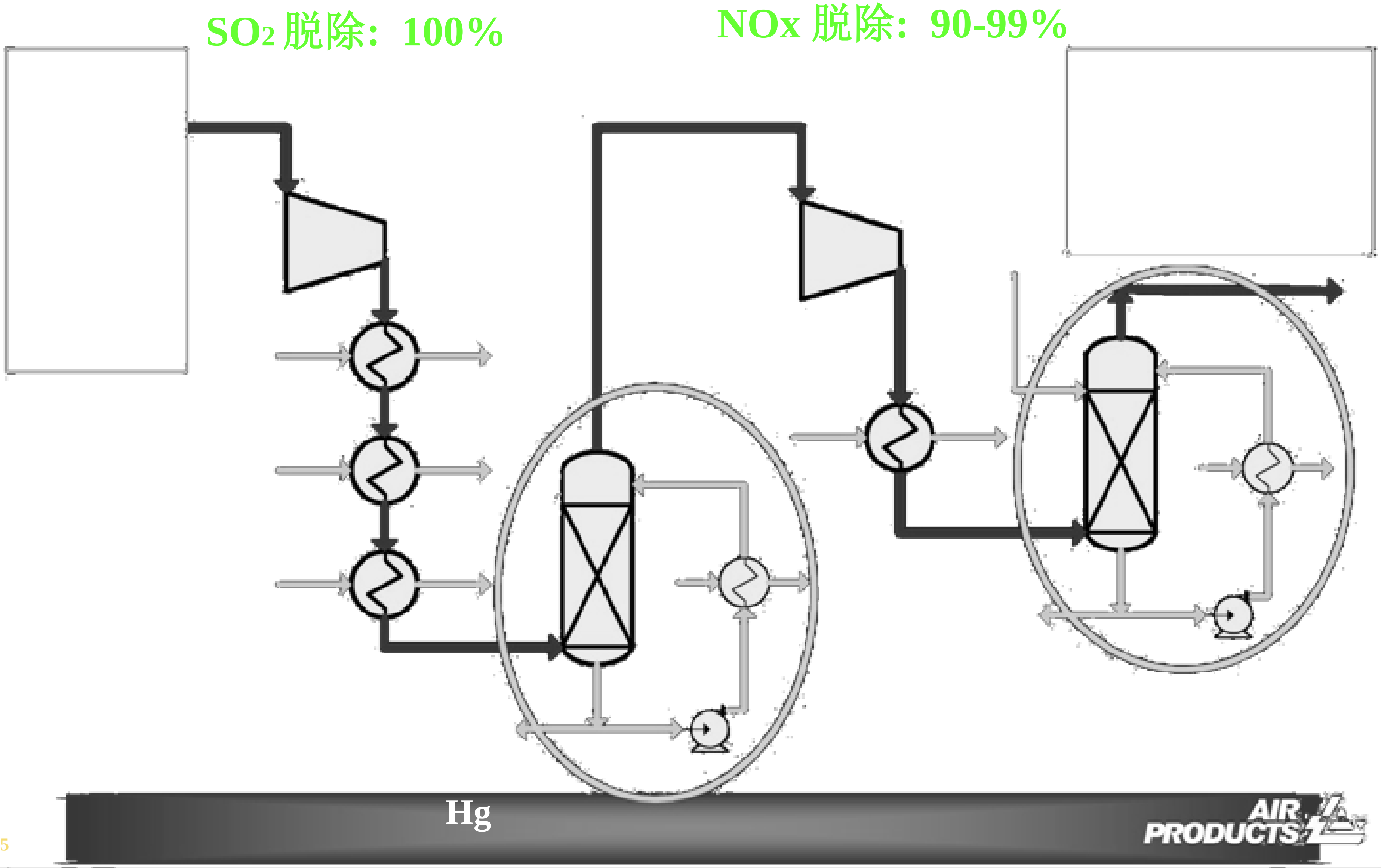
压力、反应器、停留时间都很重要。

CO_2 Compression and Purification System – Removal of SO_2, NOx and Hg



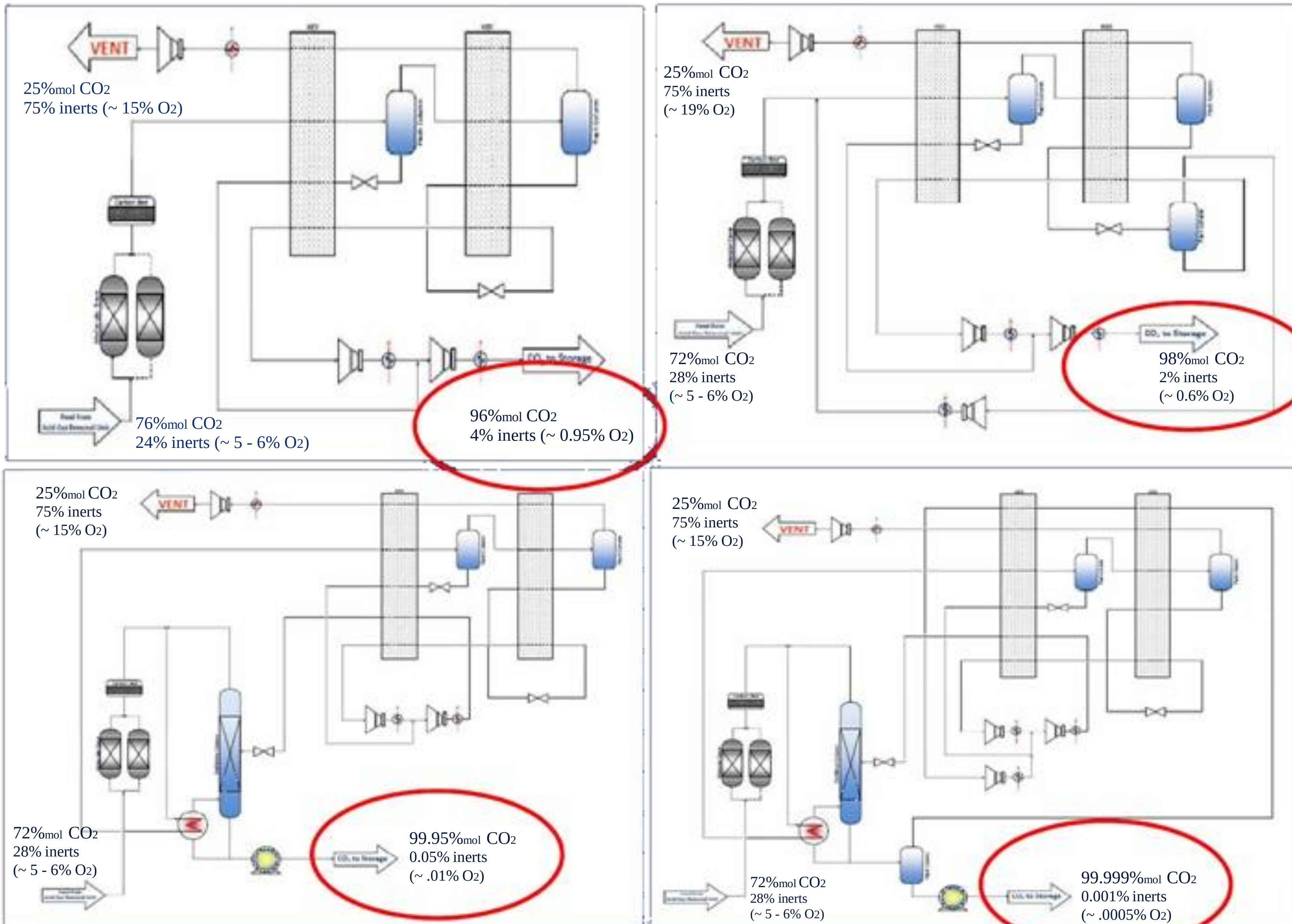
AIR PRODUCTS

CO_2压缩和净化系统
——SO_2、NOx 和Hg脱除

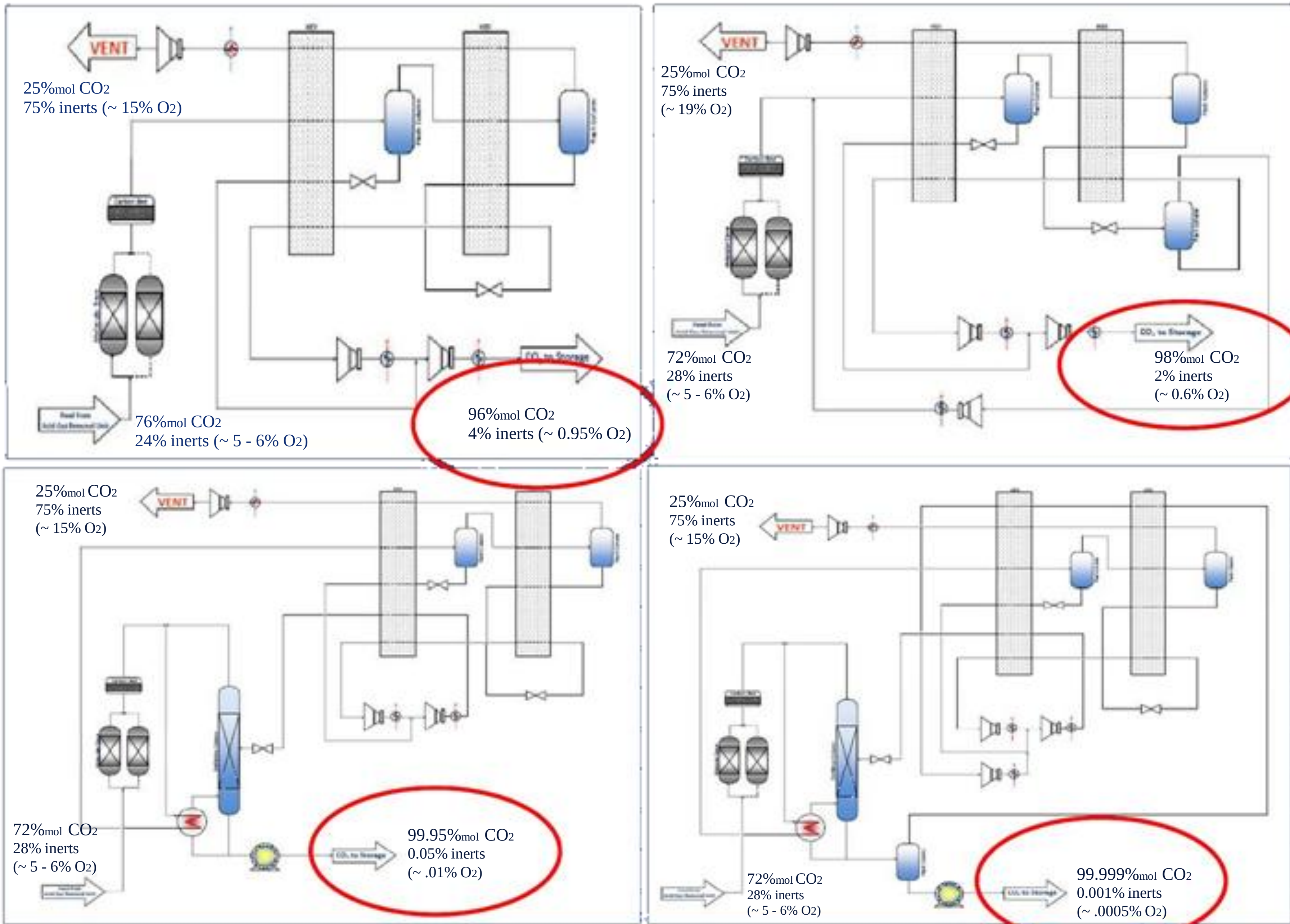


Air Product's Suggested Process Design for Various Purity…

Air Product的
针对不同纯度要求推荐的工艺设计……



AIR PRODUCTS


VENT
25%mol CO_2
75% inerts (~ 15% O_2)
76%mol CO_2
24% inerts (~ 5 - 6% O_2)
CO_2 to Storage
96%mol CO_2
4% inerts (~ 0.95% O_2)
VENT
25%mol CO_2
75% inerts
(~ 19% O_2)
72%mol CO_2
28% inerts
(~ 5 - 6% O_2)
CO_2 to Storage
98%mol CO_2
2% inerts
(~ 0.6% O_2)
25%mol CO_2
75% inerts
(~ 15% O_2)
VENT
72%mol CO_2
28% inerts
(~ 5 - 6% O_2)
99.95%mol CO_2
0.05% inerts
(~ .01% O_2)
25%mol CO_2
75% inerts
(~ 15% O_2)
VENT
72%mol CO_2
28% inerts
(~ 5 - 6% O_2)
99.999%mol CO_2
0.001% inerts
(~ .0005% O_2)

Air Product's
"Use of Membrane for further recovery of oxygen and CO_2"

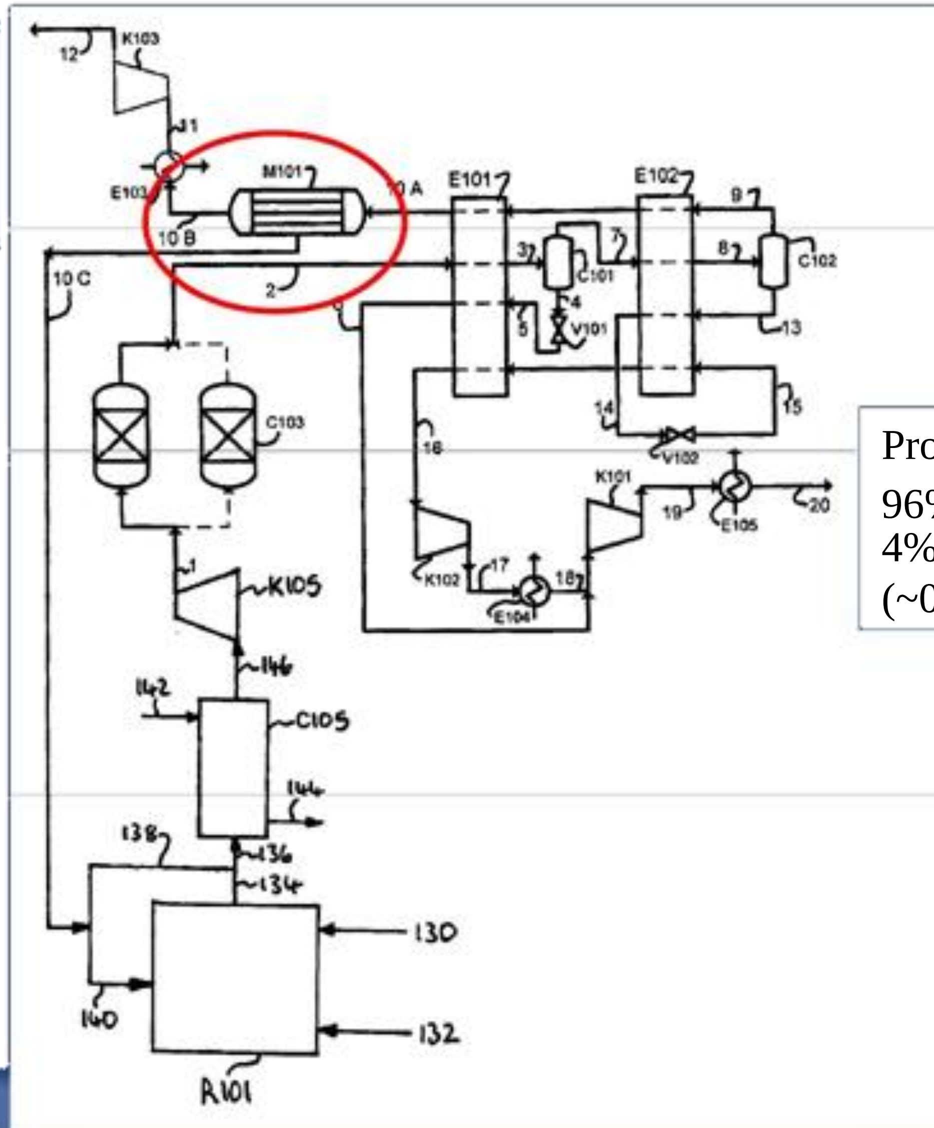
Air Product

“使用膜分离技术进一步回收O_2和CO_2”

Use of Membrane to recover CO_2 and O_2 at the vent

Vent:

7% CO_2
93% inerts
(~10% O_2)



Product

96% CO_2
4% inerts
(~0.75% O_2)

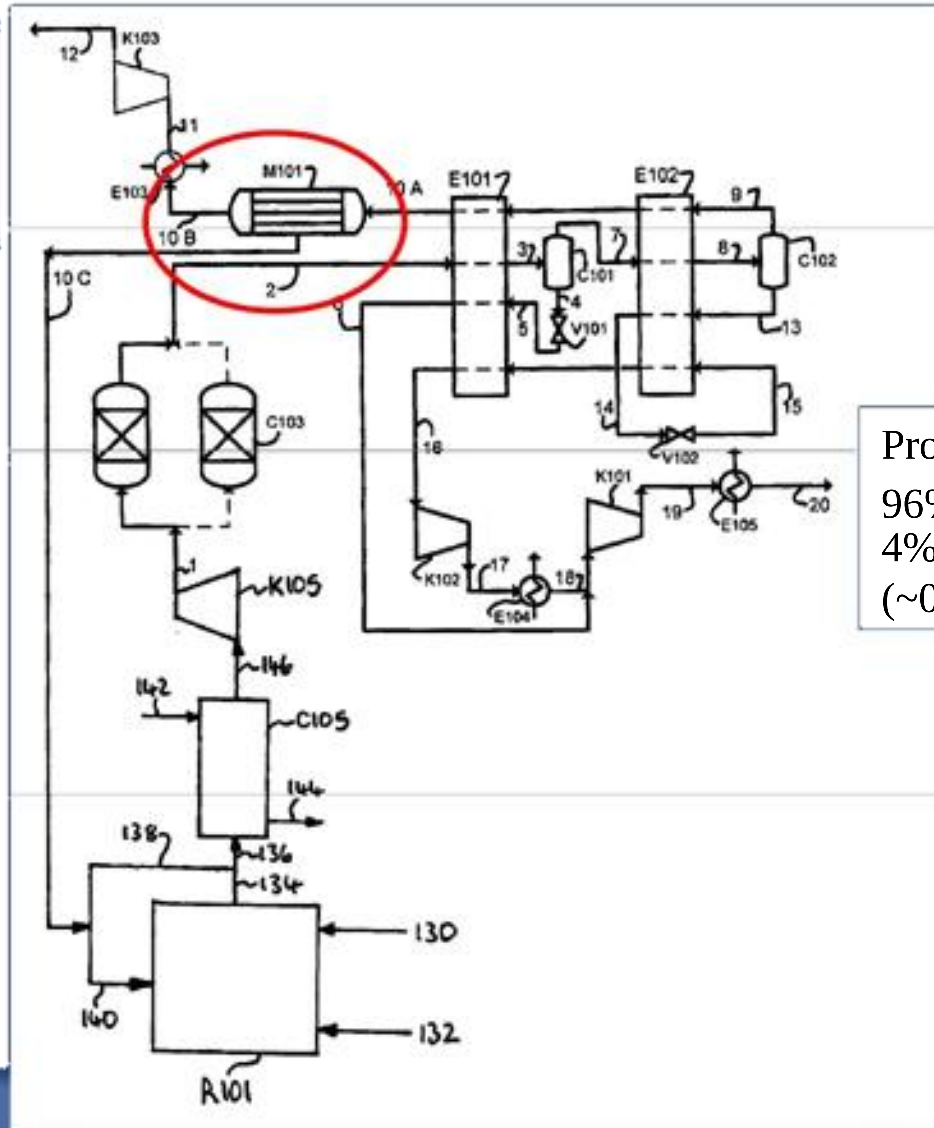
膜技术回收出口处的CO_2和O_2

Vent:

7% CO_2

93% 惰性气体

(~10% O_2)



Product

96% CO_2

4% 惰性气体

(~0.75% O_2)

Issues involving CO_2 purification process

- ***We need to establish what is appropriate and acceptable level of impurities in our CO_2 based on aspects of:***
  - Health, Safety and Environment considerations
    - What are the regulations to be established without disadvantaging any capture technology (What is acceptable!!!)
  - Quality specifications defined by transportation/delivery of CO2 to the storage sites
    - Also to consider the changes to the CO2 properties by the impurities and its possible reactions
  - Quality specifications defined by the storage CO2 for different storage options
- ***The quality of CO_2 (specific level of impurities) should be openly discussed!***

CO_2净化过程的问题

- ***建立合理、可接受的CO_2的不纯净度需要考虑：***
  - 健康、安全、环境因素
    - 制定有利于捕集技术的准则（可接受的!!!）
  - 运输到指定埋存地所要求CO_2的质量
    - 需考虑由于杂质、可能副反应造成的CO_2质量下降
  - 明确不同埋存方式所需CO_2的质量
- ***CO_2质量问题（不纯净度）应该公开讨论！***

Summary and Conclusions (CO_2 Processing Unit)

- ***Depending on the requirement of the oxygen content, processes are now available to produce CO_2 purity from 95% - 99.999%.***
  - It should be noted that higher the purity you reduce the CO_2 capture rate.
  - Higher purity means higher CAPEX and OPEX.
- ***Downstream removal of SOx and NOx depends on the taking advantage of the "lead chamber reaction" which naturally occur during wet compression.***
- ***Removal could be achieve by compressions and direct contact acid water wash. This should be demonstrated in the large scale.***

总结
(CO_2处理单元)

- ***视氧浓度要求，现有工艺能够生产纯度为 95% - 99.999% 的CO_2***
  - 应该注意的是CO_2的捕集率将随纯度要求的提高而下降
  - 高纯度意味着更高的CAPEX 和OPEX
- ***下游SOx和NOx的脱除取决于“铅室反应”的利用，这些反应在湿压缩中自然发生***
- ***可以通过压缩和酸洗实现脱除，这应该大规模示范。***

SUMMARY AND CONCLUSIONS

- BURNER AND BOILER DEVELOPMENT

- OXYGEN PRODUCTION

- CO2 PROCESSING UNIT

结论

- 燃烧器和锅炉发展
- 制氧
- CO_2 处理单元

Burner & Boiler Development

- ***Demonstration via large scale burner testing is essential to the development of oxy-combustion.***
- ***Key areas of R&D should focus on:***
  - Heat transfer and flame properties
  - Coal devolatilisatoin and char combustion
  - Slagging, fouling deposition characteristics
  - Emissions (sulphur chemistry, PM and Hg + trace metals)
- ***Development in CFD modelling is an essential tools to help design of future burners and boilers.***

燃烧器和锅炉发展

- *大规模燃烧器示范试验是富氧燃烧的发展基础*

- *研发的关键重点在:*
  - 传热和火焰特性
  - 煤挥发分析出与焦炭燃烧
  - 结渣、积垢特性
  - 污染物排放(硫化学, PM和Hg + 微量金属)

- *发展CFD模拟软件有助于未来燃烧器和锅炉的设计*

ASU & CPU

- ***Air Separation Unit : improvement in performance is available now***
- ***CO2 CPU : feasibility is confirmed but design will remain conservative until pilot plants are started ; significant improvements in performance are achievable for cryogenic unit***
- ***Integration of ASU and CO_2 Processing Unit in the overall oxyfuel combustion plant are key to achieve high efficiency and low capital expenditure***
- ***Should also consider looking at novel oxygen production***

ASU & CPU

- *空分单元：现在可以进行性能改进*
- ***CO_2 CPU**：可行性已得到确认，但在中试厂启动前仍需谨慎设计；依靠深冷单元 可以显著提高性能*
- *富氧燃烧电厂中，**ASU**和**CO_2**处理单元的集成是达到高效低投资的关键。*
- *同时应该考虑新型制氧技术*

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Concluding Remarks

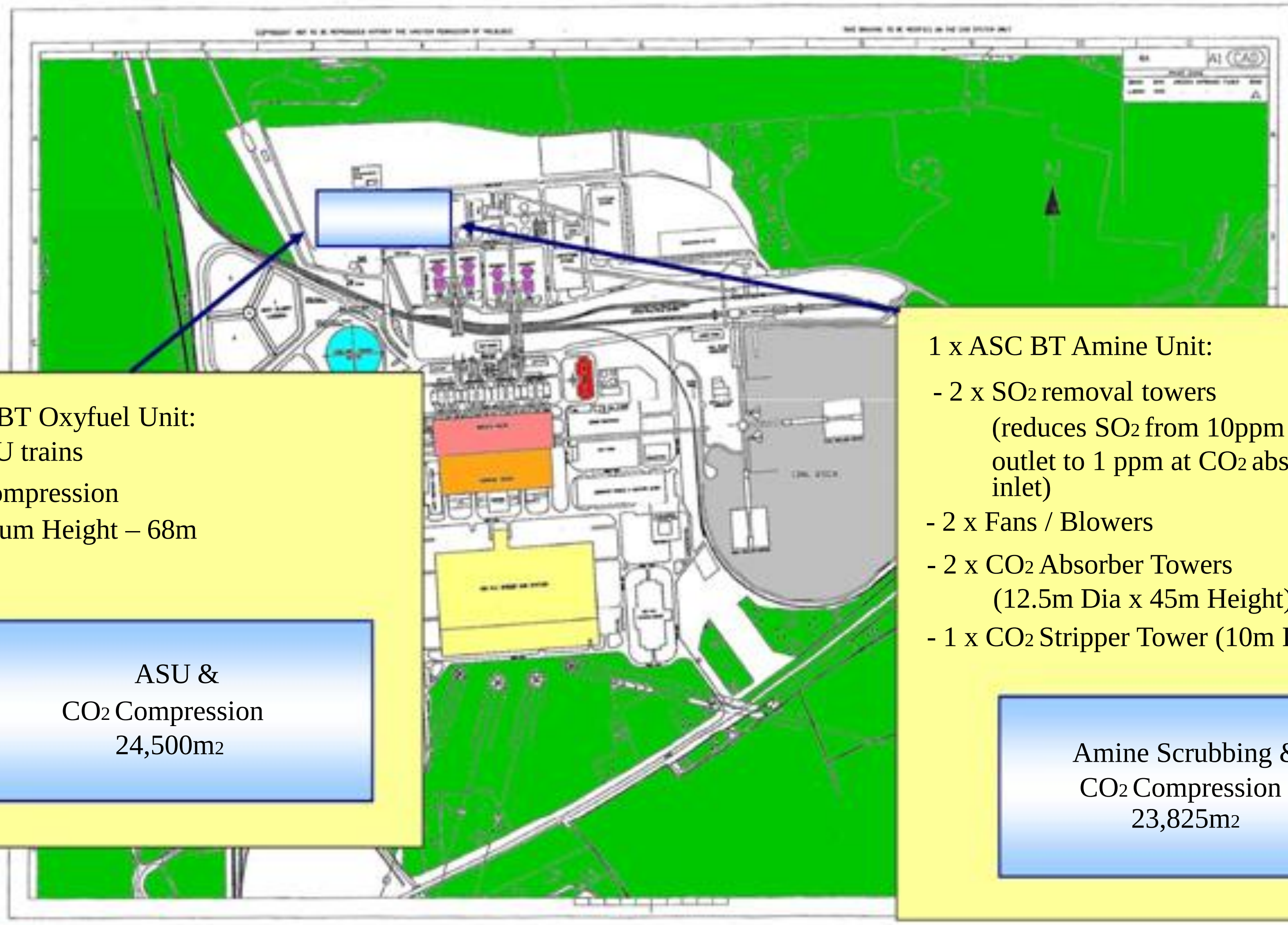
- *Oxyfuel Combustion Technology is a viable option for any coal fired power plant with CO_2 Capture.*
- *Oxyfuel Combustion Technology is an option for new build or retrofit cases.*
- ***We need to demonstrate Oxyfuel Combustion Technology to build our confidence.***
- *Business sense, it could have a simple business model for power generation companies wherein the operation of the ASU and CO_2 processing could be outsourced with a long term supply contract from the industrial gas companies.*

结束语

- *对于带有CO_2捕集的任何燃煤电厂而言，富氧燃烧技术是一种切实可行的选择*
- *富氧燃烧技术适宜于新建或改建*
- ***我们需要示范富氧燃烧技术来建立信心***
- *从商业意识角度讲，发电公司可以有一个简单的商业模式，即通过与工业气体公司签订长期供给合同，实现ASU的运行和CO_2处理单元的外包。*

Footprint of Capture plant – DTI Project 407

- Oxyfuel and amine scrubbing have similar footprints



1 x ASC BT Oxyfuel Unit:

- 2 x ASU trains
- CO_2 Compression
- Maximum Height – 68m

ASU &
CO_2 Compression
24,500m^2

1 x ASC BT Amine Unit:

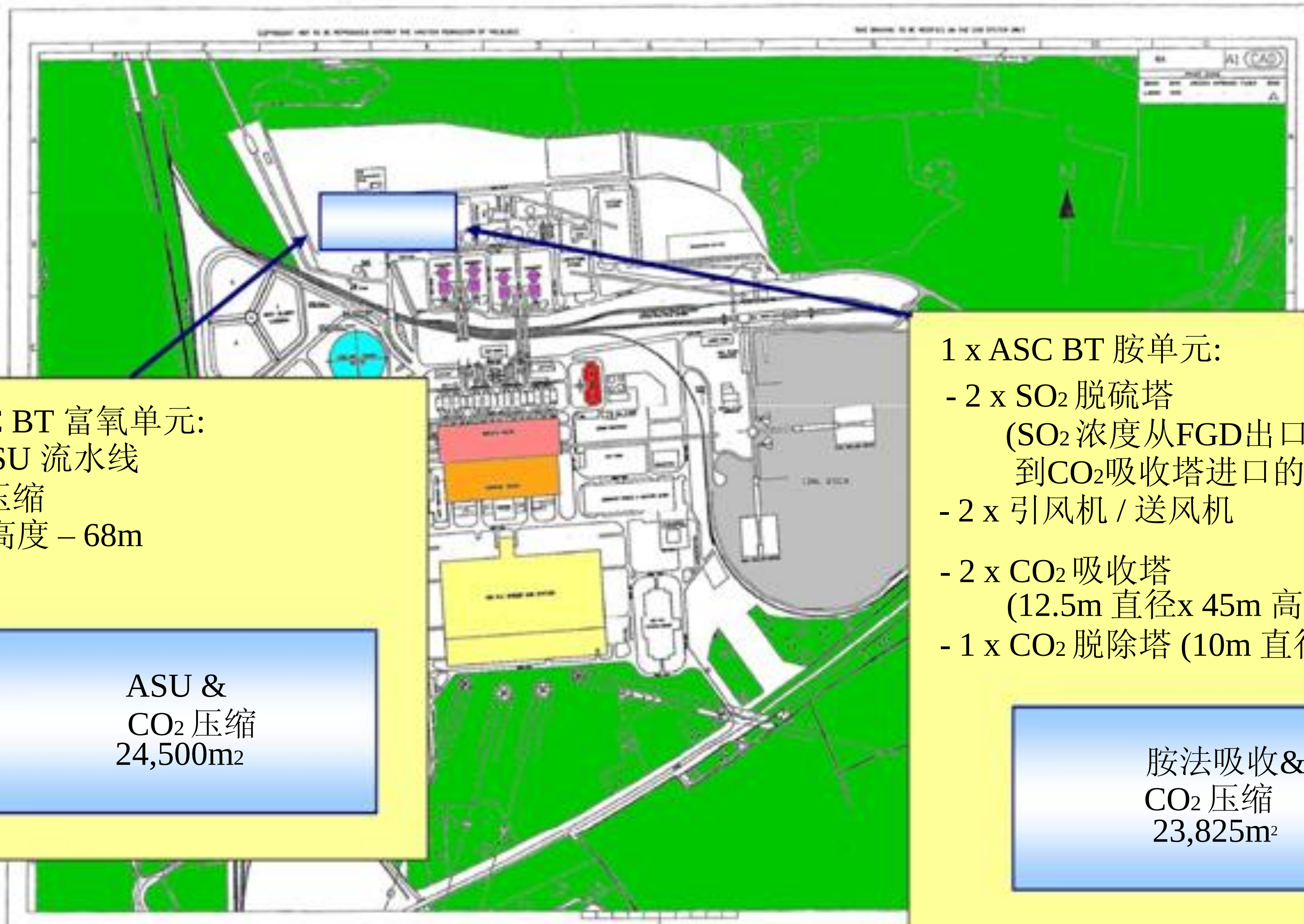
- 2 x SO_2 removal towers
  (reduces SO_2 from 10ppm at FGD outlet to 1 ppm at CO_2 absorber inlet)
- 2 x Fans / Blowers
- 2 x CO_2 Absorber Towers
  (12.5m Dia x 45m Height)
- 1 x CO_2 Stripper Tower (10m Dia)

Amine Scrubbing &
CO_2 Compression
23,825m^2

Doosan Babcock Energy

发展历程– DTI 项目 407

- 富氧燃烧与胺法吸收有类似的历程



1 x ASC BT 富氧单元:
- 2 x ASU 流水线
- CO_2 压缩
- 最大高度 – 68m

ASU &
CO_2 压缩
24,500m2

1 x ASC BT 胺单元:
- 2 x SO_2 脱硫塔
  (SO_2 浓度从FGD出口的 10ppm 降低到CO_2吸收塔进口的1 ppm）
- 2 x 引风机 / 送风机
- 2 x CO_2 吸收塔
  (12.5m 直径x 45m 高)
- 1 x CO_2 脱除塔 (10m 直径)

胺法吸收&
CO_2 压缩
23,825m2

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Thank you

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