

碳捕获和封存在水泥行业技术选择

Technical Options for CCS Applications in the Cement Industry

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CCS Options for Energy Intensive Industry Workshop

Beijing Xinyuan Hotel

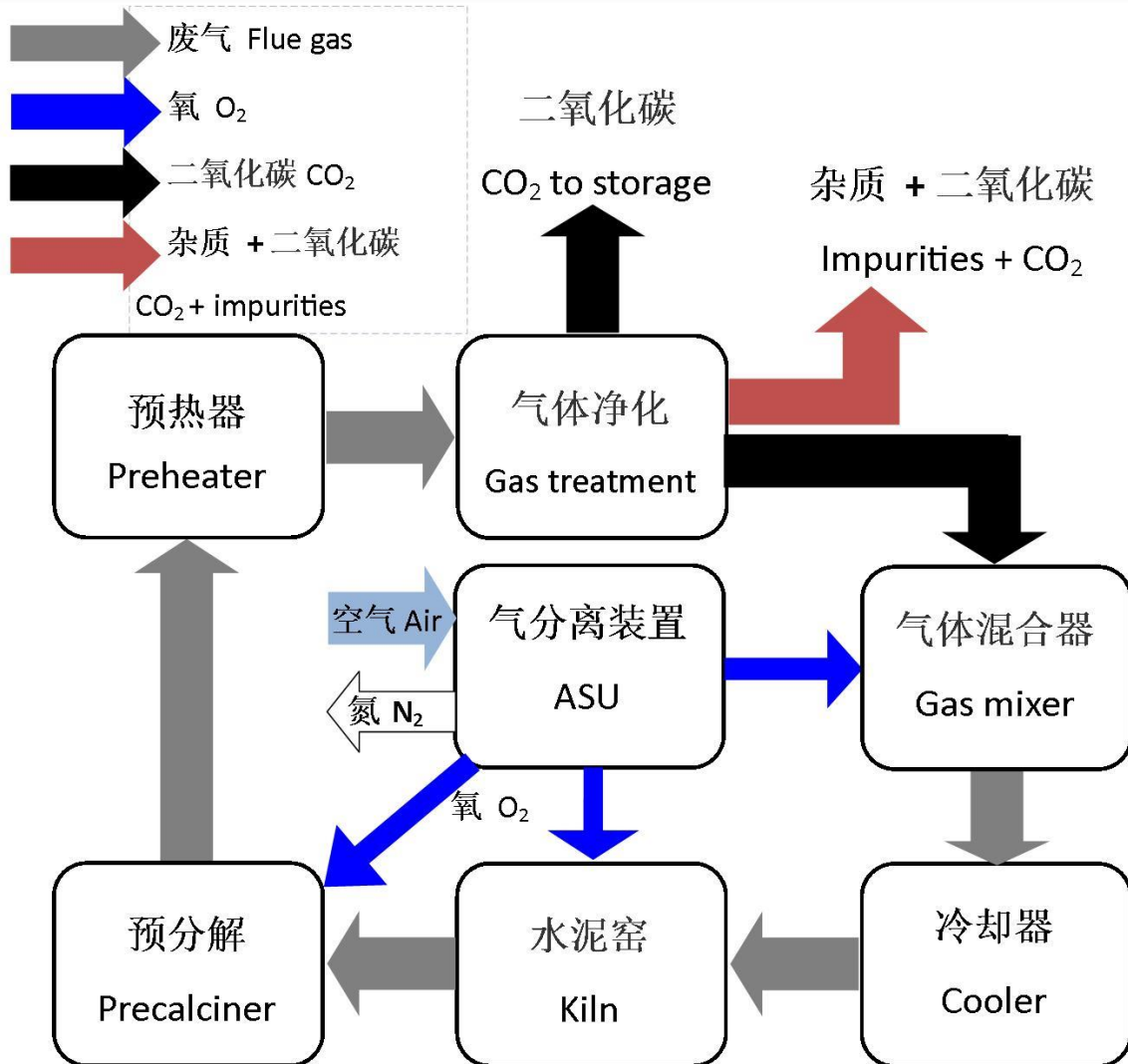
5th December 2013

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富氧燃烧 Oxyfuel Combustion



1. 氮氧分离, 氧气用于煤炭燃烧, 同时循环一部分二氧化碳用于控制火焰温度。
2. 中等复杂度-二氧化碳纯度易于受来自空气中的氮气的污染。
3. 窑中气体CO₂含量通常>80%

1. O₂ and N₂ separated, O₂ used to burn the coal, with some CO₂ recycled from the exhaust to moderate flame temperature.
2. **Moderate complexity** – susceptible to contamination of CO₂ by N₂ from the atmosphere.
3. Atmosphere in kiln generally >80% CO₂

低温分离 Cryogenics

低温空气分离技术先将空气冷却到空气的沸点，之后再将液态氧气与气态的氮气分离。

1. 高电力需求：240 千瓦时/吨 O_2 (160 千瓦时是极限)
2. 成品技术 – 十分成熟的技术（不过任然有一些安全问题）

Cryogenic air separation cools air down to the boiling point of oxygen, and liquid oxygen is separated from gaseous nitrogen

1.High electricity demand: 240 kWh/t O_2 (160 kWh is the limit)

2.Off-the-shelf technology – very **proven technology** (but still has some safety issues)

高温氧气传送膜

High-temperature oxygen transport membranes

氧气从压缩空气送入回收烟气

1. 氧气输送膜（OTMS）操作时必须保持高于800°C 的高温。
2. 氧的分压必须保持，以使氧气通过。
3. 目前最好的膜不能暴露于烟道气中 – 这增加了能量需求
4. 需要大型设备：渗透性在0.1-1克/平方米. 秒的范围

Oxygen is passed from compressed air into recycled flue gases

1. Oxygen transport membranes (OTMs) must be kept **above 800°C when in operation**
2. An oxygen partial pressure must be maintained to cause the oxygen to pass through
3. The current best membranes cannot be exposed to flue gases – this **increases the energy requirements**
4. **Large apparatus required:** permeability is in the range of 0.1-1 g/m².s

富氧水泥厂的主要优点

Major benefits of oxy-fuelled cement plants

- | | |
|---|--|
| 1. 降低了水泥窑的燃料需求 | 1.Reduces the fuel requirements of the kiln |
| 2. 可移除几乎所有的二氧化碳 | 2.Can remove virtually all of the CO ₂ |
| 3. 基本消除煤磨的爆炸风险 | 3.Explosion risk in coal mill virtually eliminated |
| 4. 富集至30-35% O ₂ 氛围可以将窑炉产能提高25-50% | 4.Enrichment to 30-35% O ₂ atmosphere can increase kiln capacity by 25-50% |

富氧水泥厂的主要缺点

Major drawbacks of oxy-fuelled cement plants

1. 氧分离仍然是昂贵的，因为它需要使用了大量的电力

1. 一个3000吨/天（100万吨/年）的工厂需要7-8kg O₂/秒

2. 由于烧结原因，在高浓度CO₂下煅烧石灰将使其表面面积降低高达66%。这可能会影响钙硅酸盐的形成。

3. 该水泥厂必须密闭 - 这包括水泥窑！

4. 需要对冷却器，分解炉和预热器进行昂贵的改进

1. Oxygen separation is still **expensive** because it uses lots of electricity

1. A 3000 t/d (1Mt/y) plant requires 7-8kg O₂/s

2. Calcination in high-CO₂ atmospheres **reduces the surface area of lime by up to 66%** due to sintering. This may affect the formation of calcium silicates

3. The **cement plant must be airtight** – this includes the kiln!

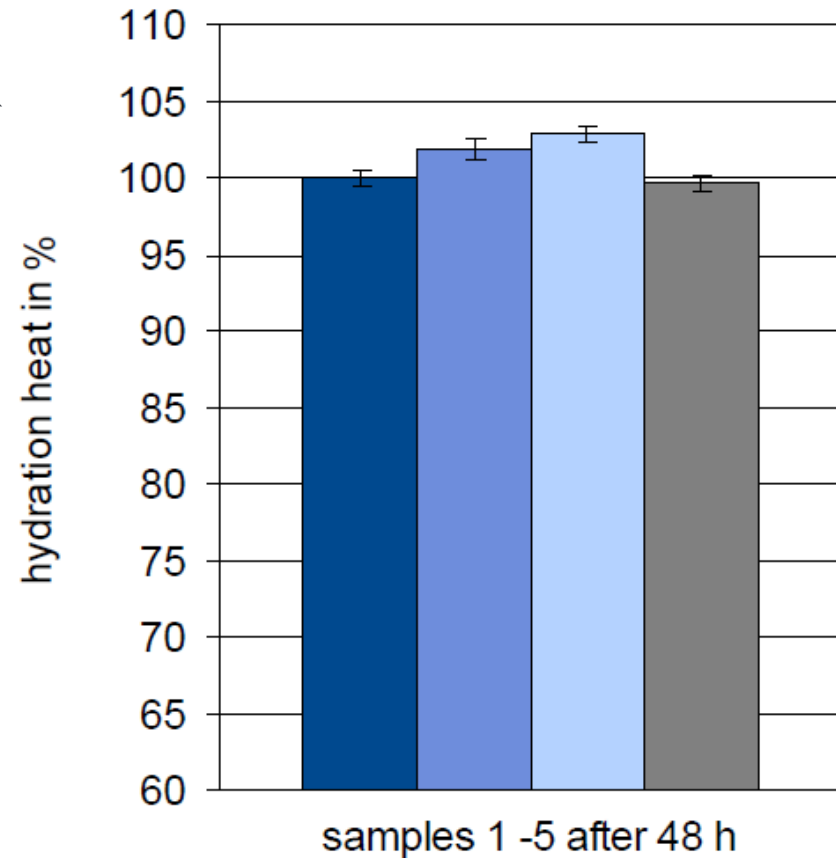
4. Extensive modifications to the cooler, precalciner and preheaters required

富氧条件下水泥的水化特性

Hydration characteristics of oxy-fuel cement

富氧条件下的水泥的水化似乎比标准水泥稍微好一点 - 即高反应性

The hydration of oxyfuel cement seems to be slightly better than for standard cement – i.e. **high reactivity**

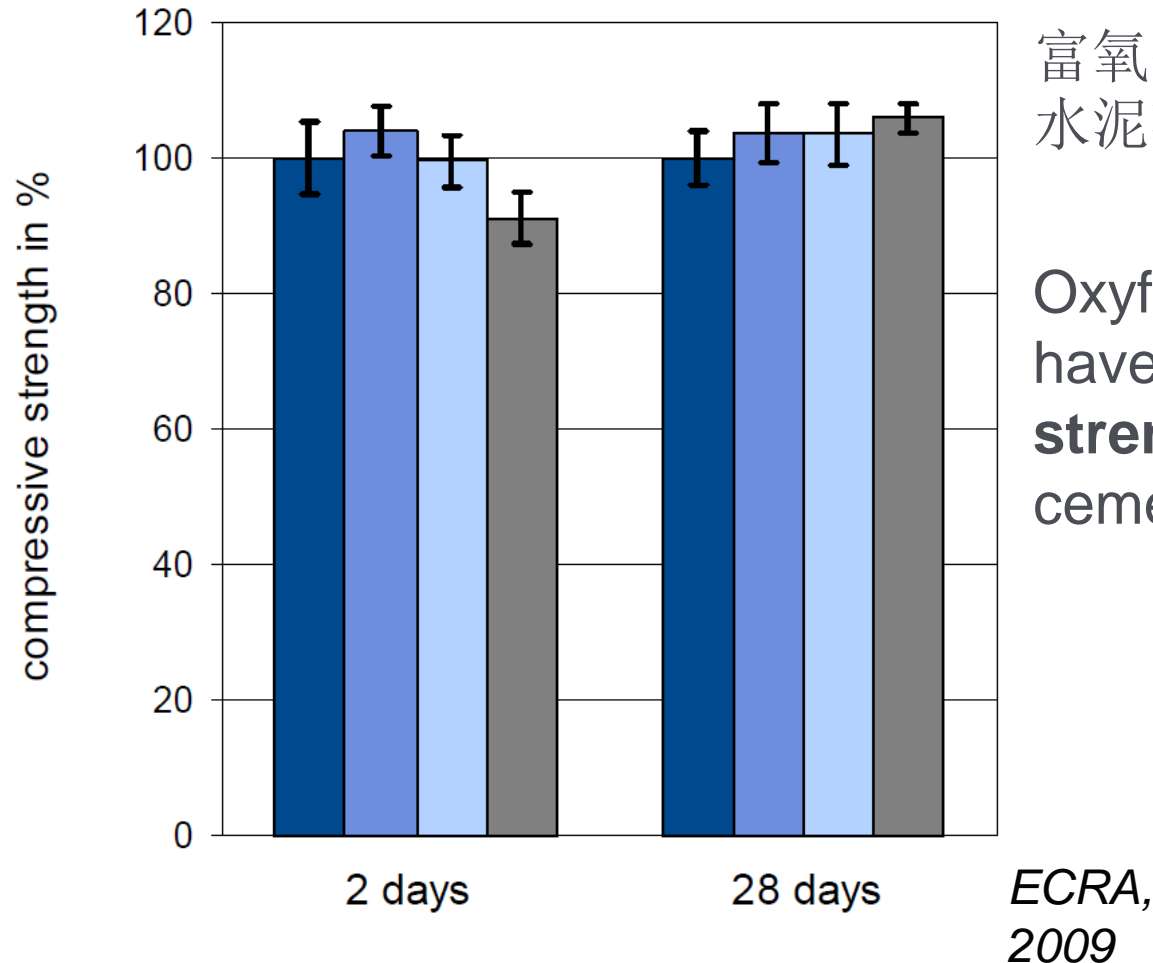


*ECRA,
2009*



富氧条件下水泥的抗压强度

Compressive strength of oxyfuel cement



富氧条件下的水泥似乎与标准水泥有类似的抗压强度

Oxyfuel cements seem to have **similar compressive strengths** to standard cements

■ Standard condition ■ Oxyfuel condition
■ Burning: CO2/ Cooling: Standard ■ Burning: Standard/ Cooling: CO2

其它重要实验结果

Other important laboratory results

1. 无方解石（碳酸钙）在熟料中检测到 – 没有再碳酸化在高二氧化碳环境中发生
2. 在alite/belite比率并没有显著差异- alite的分解水平在十分相似
3. 由于二氧化碳环境而得到的更好的冷却效果没有在富氧条件下的水泥样品中观测到

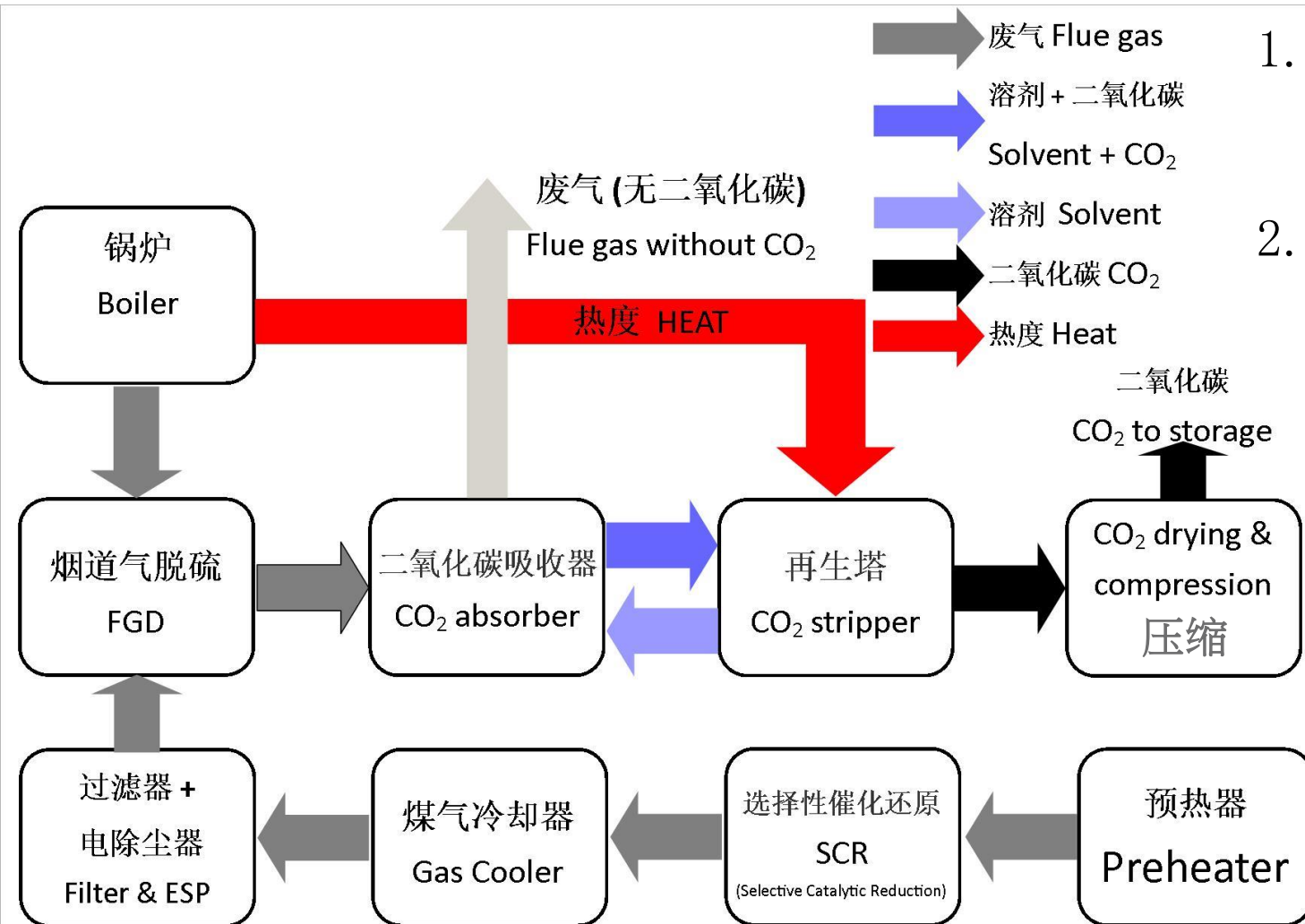
总体上来说，富氧条件下的水泥和标准水泥之间只有十分微小的不同

- 1.No calcite (CaCO_3) was detected in the clinker – no recarbonation took place in the high CO_2 atmospheres
- 2.No significant variations in the alite/belite ratio were identified – similar levels of decomposition of alite in both oxyfuel and standard cements
- 3.Effects of better cooling due to CO_2 atmosphere not observed in most oxyfuel samples

Overall, the differences between standard and oxyfuel cement properties are very small.

燃烧后捕获-液氨脱除

Post-combustion capture – amine scrubbing



1. 末端治理技术-
可以很容易地改
装连接到水泥厂
2. 需要大量的热能
输入来再生溶剂

1. 'End of pipe' technology – can be easily retrofitted to the cement plant

2.Requires large heat input to regenerate the solvent

液氨脱除技术的优缺点

Benefits and drawbacks of amine scrubbing technology

1. 在电力行业是“市场领导者” – 虽然已经面世数十年，但必须扩大规模
2. 末端治理方式 – 它可以连接到一个现有的水泥厂
3. 可以与水泥厂独立运行 – 灵活

-
1. 二氧化碳捕获之前必须把烟道气中的二氧化硫，氮氧化物和粉尘去除
 2. 大量蒸汽需求
 3. 大量的资金成本 – 价格昂贵

1.The ‘**market leader**’ in the power sector – it has been available for decades but must be scaled up

2.End-of-pipe solution - it can be attached to the back of an existing cement plant

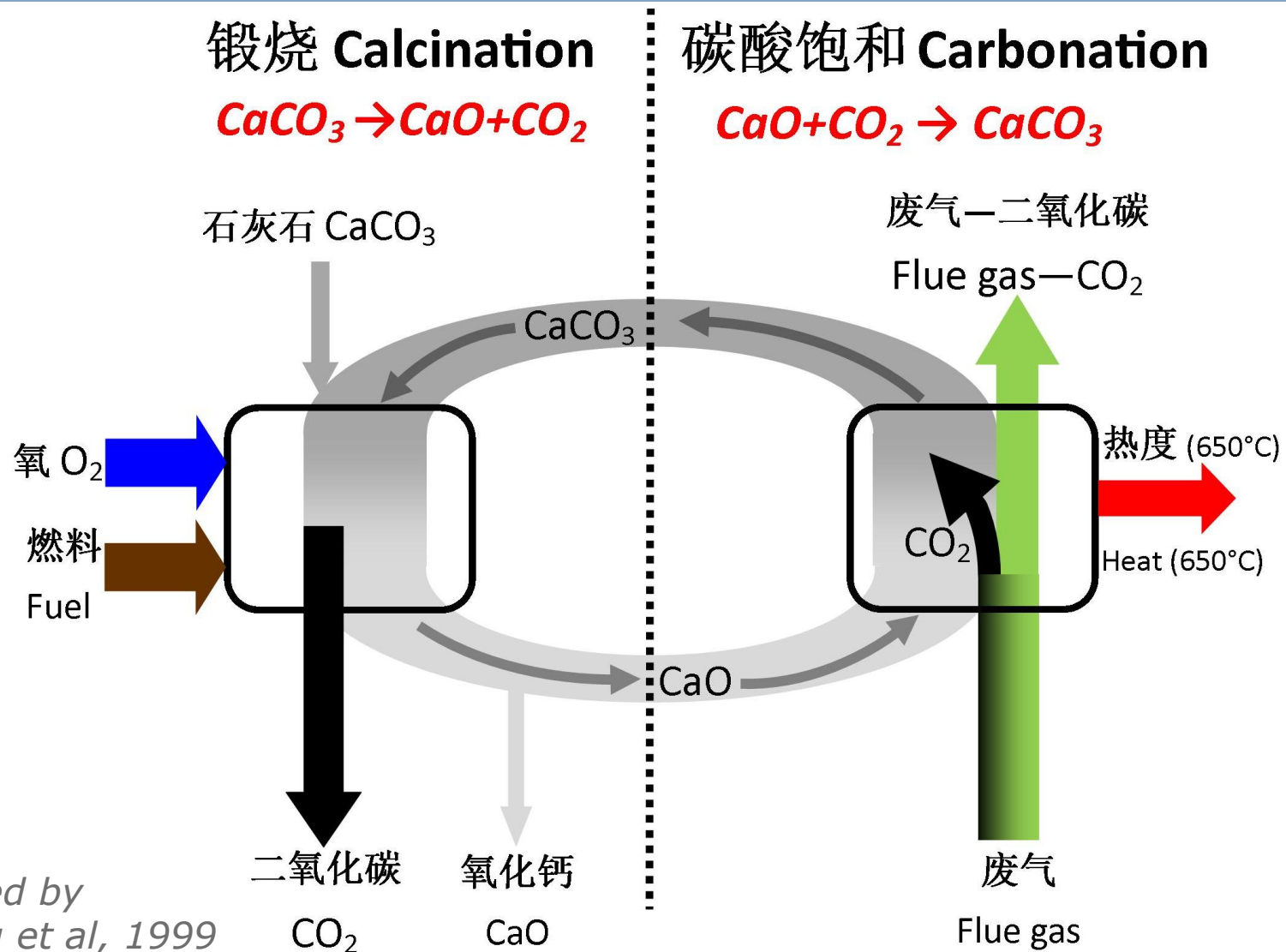
3.Can be run independently from the cement plant - **flexible**

1.SO₂, NO_x and dust must be removed from the flue gas before CO₂ capture

2.Large steam requirements

3.Large capital cost - **expensive**

新兴技术 - 钙基吸收剂循环过程 Emerging methods - Calcium Looping



Proposed by
Shimizu et al, 1999

新兴技术 - 钙基吸收剂循环过程 Emerging methods – Calcium Looping

1. 废品是氧化钙（+灰），可以运用于水泥生产
2. 虽然煤的消耗量增加，但废弃能源可以用于发电
3. 空气分离装置的大小只有富氧厂中的四分之一
4. 燃烧后工艺：具有改装的可能性，但如果结合水泥厂则有大收益

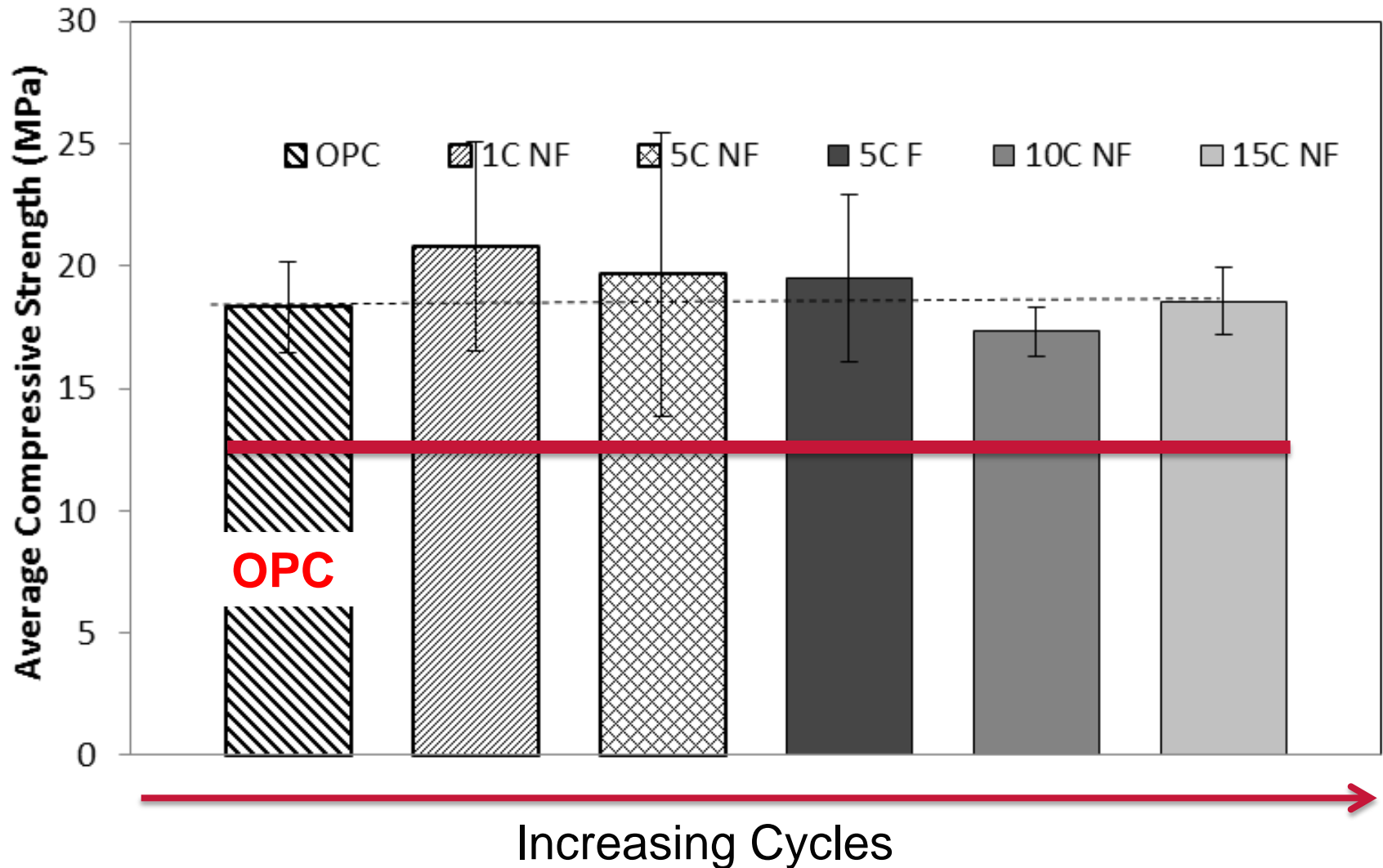
1. Waste product is CaO (+ash) which can be used in cement manufacture

2. Coal consumption is increased but **electricity can be generated** from the waste energy

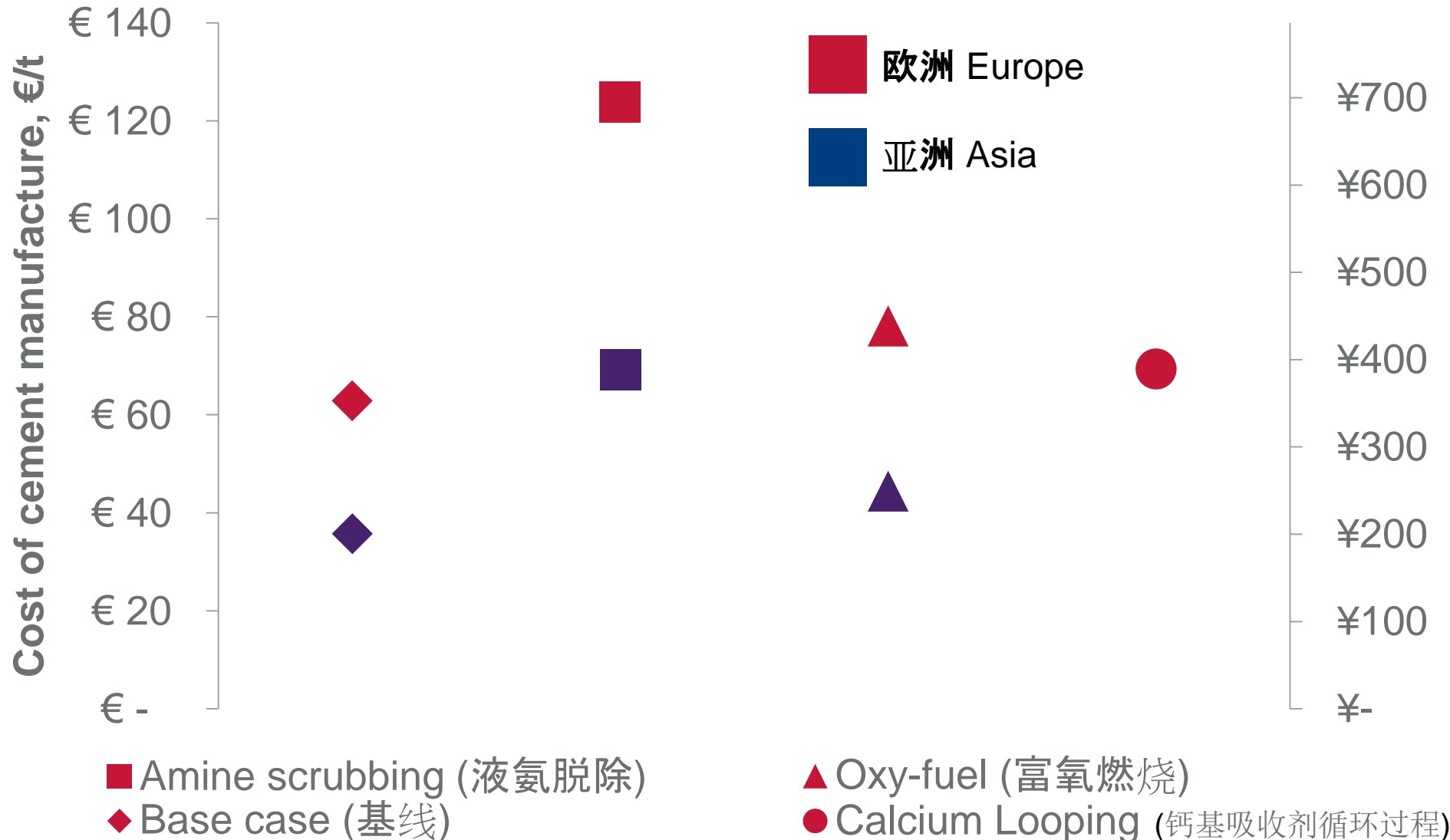
3. Air separation unit is only $\frac{1}{4}$ of size in oxy-fuel plant

4. Post-combustion process: **retrofit possible**, but greater benefits if integrated with the cement plant

钙基吸收剂循环过程 - 耐压强度 Calcium Looping – Compressive Strength



二氧化碳捕获和储存运用于水泥厂的成本 (¥/吨产品) Costs of carbon capture at cement plants (£/t cement)



二氧化碳捕获和储存运用于电厂和水泥厂的主要区别

Key differences between CCS at power stations and cement plants

1. 燃烧前捕获对水泥厂并不有效
 1. 只有40%的CO₂可以通过这种方法被捕获
2. 水泥质量增加了电厂没有的一个层面的问题
3. 利用水泥厂的废弃物燃料会导致不同的污染问题
4. **规模经济** – 电站的输送量通常较大，因此相对于水泥厂，电厂可以达到更高规模的经济体

1.Precombustion capture is not effective at cement plants

- 1.Only 40% of CO₂ can be captured via this method

2.Cement quality adds another dimension to the problem that the power sector does not have

3.Use of waste fuels in cement plants causes different contaminant problems

4.Economies of scale – power stations are usually larger emitters, and so can attain higher economies of scale than cement plants

潜在研究项目

Potential research projects

1. 富氧条件下生成煤渣的性质
2. 对二氧化碳捕捉和储存结合水泥制造厂的成本研究
3. 运用不同技术（富氧，液氨脱除，钙基吸收剂循环过程）的中间试验工厂
1. Properties of clinker produced in oxy-fuel and calcium looping conditions
2. Costs of cement plants with CCS in China
3. Pilot plants using the different technologies (oxyfuel, amine scrubbing, calcium looping)
4. Better quantification of the lifecycle of cement with CCS, including with waste biological fuels

致谢 Acknowledgements

感谢北京的主办方给与这次演讲的机会

同样感谢我的赞助方：

- 西麦斯AG研究团队
- Grantham气候变化研究所
- 欧洲创新技术学院气候知识和创新协会

Thank you to my hosts here in Beijing for this opportunity

Thank you also to my sponsors:

- Cemex Research Group AG
- Grantham Institute for Climate Change
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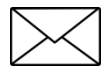


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Thank you for your attention

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