CCUS在钢铁工业中应用

Application of CCUS in Steel Industry

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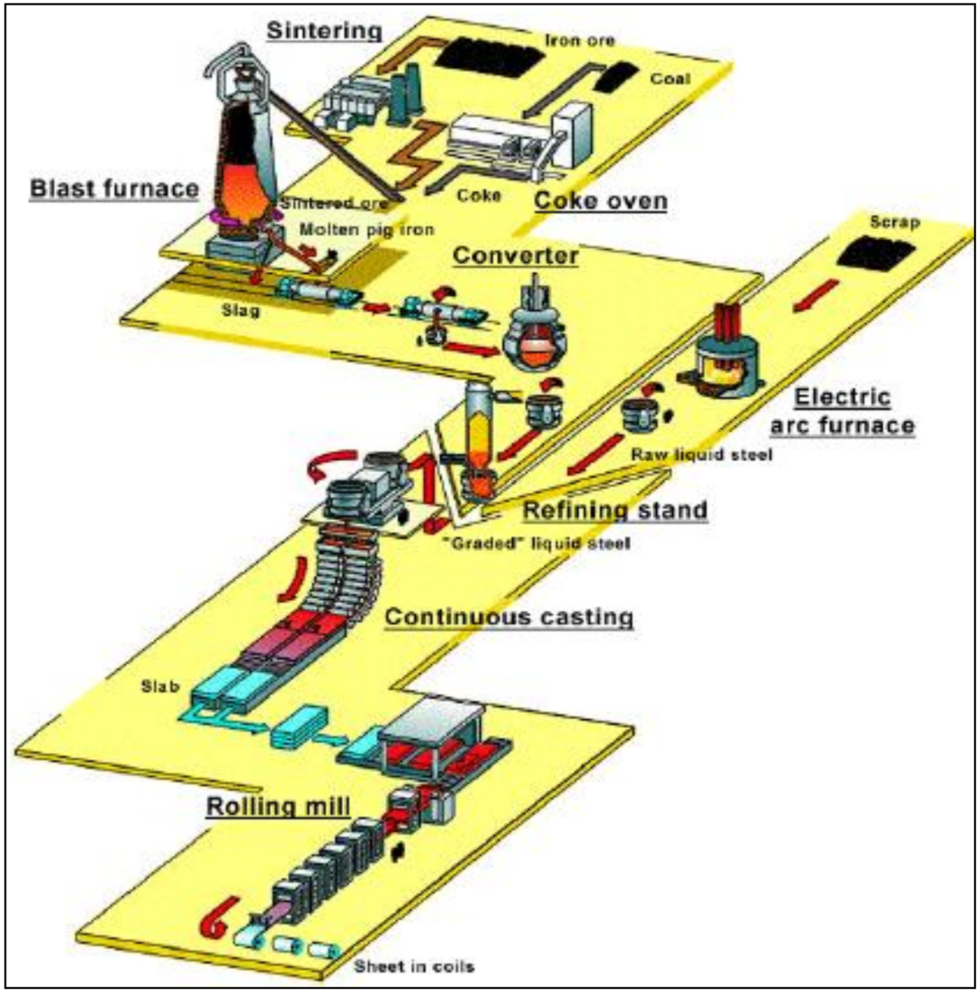
钢铁工业二氧化碳排放量巨大
Huge CO_2 emissions in steel industry

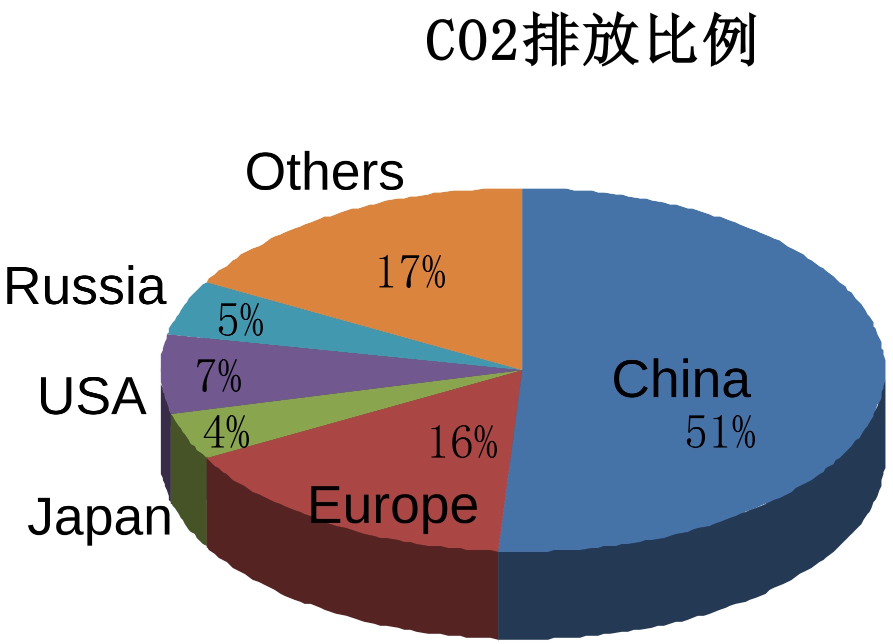


钢铁工业温室气体排放主要为CO_2。国际钢铁协会指出全球钢铁工业温室气体排放量约占全球温室气体排放总量的3.2%。

CO_2 is the main greenhouse gas in iron&steel industry. International Iron&Steel Association pointed out that the greenhouse gas emissions of global steel industry accounted for 3.2% of global greenhouse gas emissions.

中国钢铁工业二氧化碳排放引起世界关注

The CO_2 emission in I&S industry in china caused global attention



各国钢铁行业CO_2排放状况

2012年中国钢铁产量达到7.16亿吨,占全球钢产量的46.3%；CO_2排放量约占全球钢铁行业CO_2排放量的50%。

Chinese steel production in 2012 was 0.716 billion tons, accounting for the 46.3% of the global steel output; CO_2 emissions accounted for 50% of the global steel industry

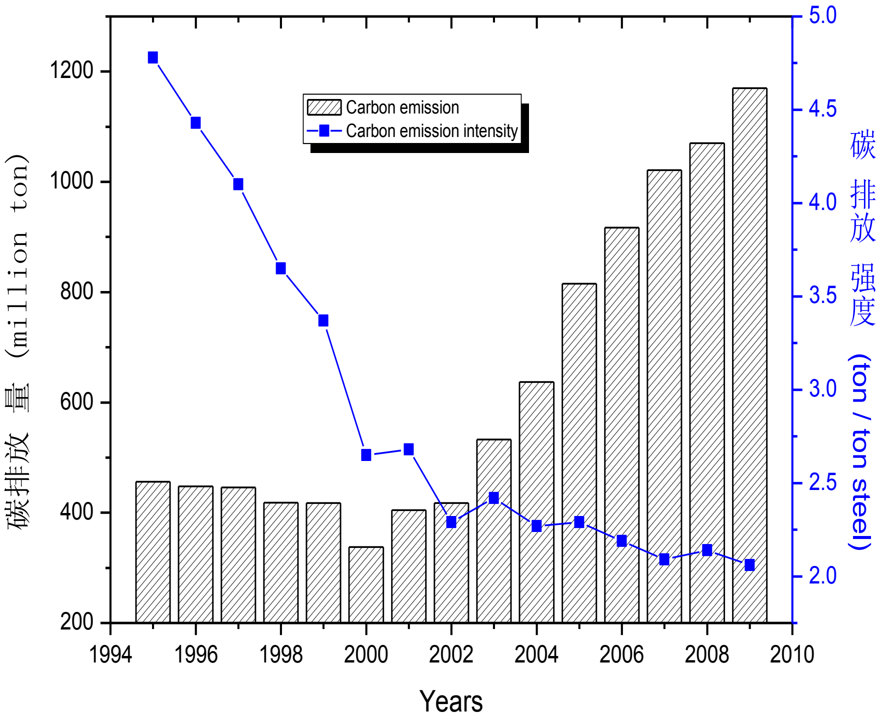
- 摘自国际钢铁协会的内部报告，但估算方法不详。

中国钢铁工业CO_2排放与世界先进水平相比仍有一定差距

The gaps compared with the top level of the world

中国钢铁行业CO_2排放总量增加/但碳排放强度持续降低。

The CO_2 emissions of China steel industry increased, but the carbon emission intensity decreased.



中国钢铁行业CO_2排放量与强度

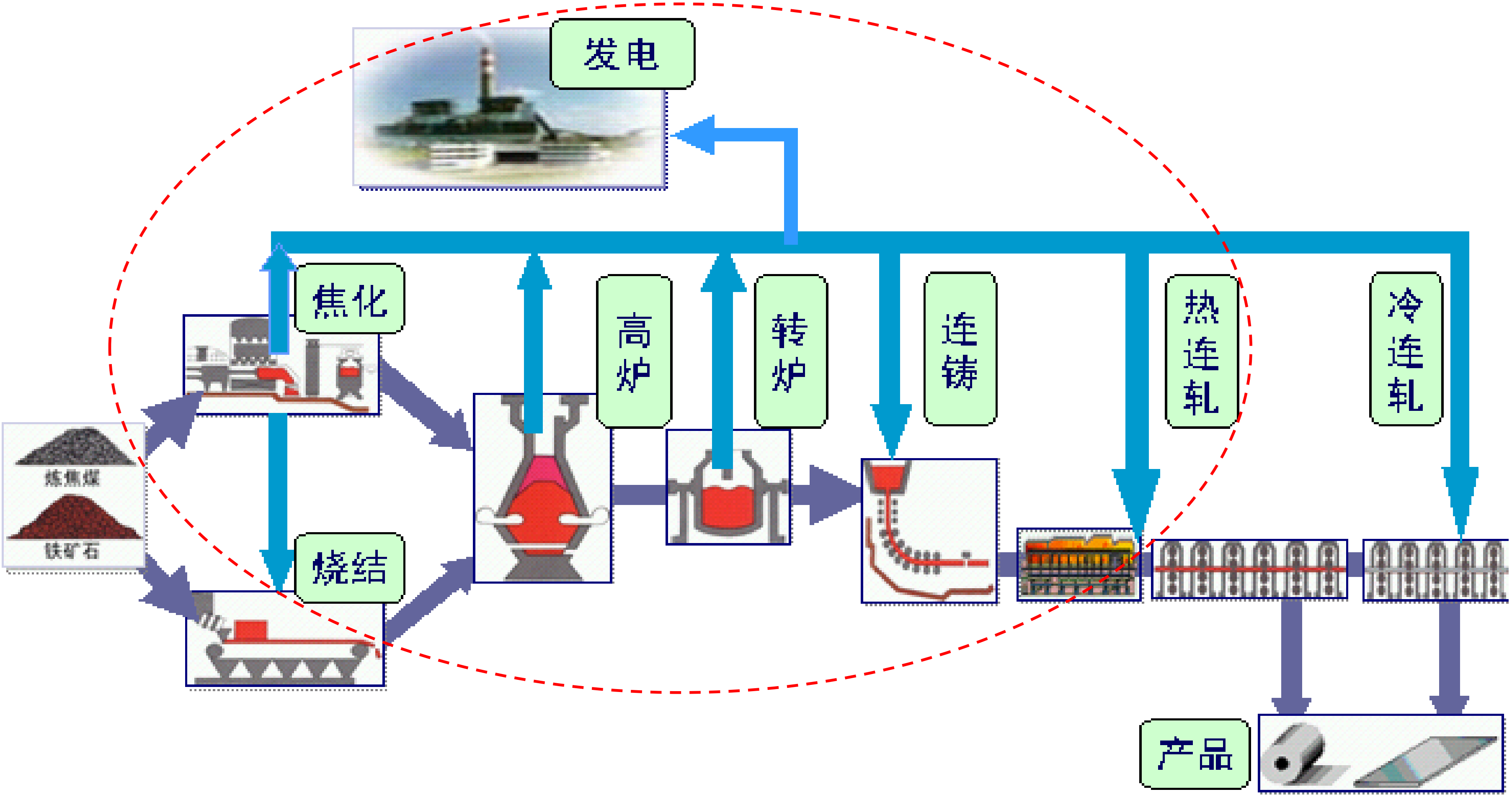
来源	CO_2排放强度 tCO_2/t	备注（2010年前数据）
日本住友金属 (Sumitomo Metal)	1.95	能源消耗
	2.09	能源+熔剂消耗
日本新日铁 (Nippon Steel)	1.82	能源消耗
韩国POSCO	2.19	包括2.12 tCO_2/t-s的直接排放和0.07 tCO_2/t-s的间接排放
国际钢铁协会 (IISA)	1.7	国际钢铁工业可持续发展指标（未注明计算范围）

国际先进钢铁企业CO_2排放强度

–国际钢铁界还没有统一的CO_2排放量计算方法

长流程钢铁生产过程CO_2主要排放单元

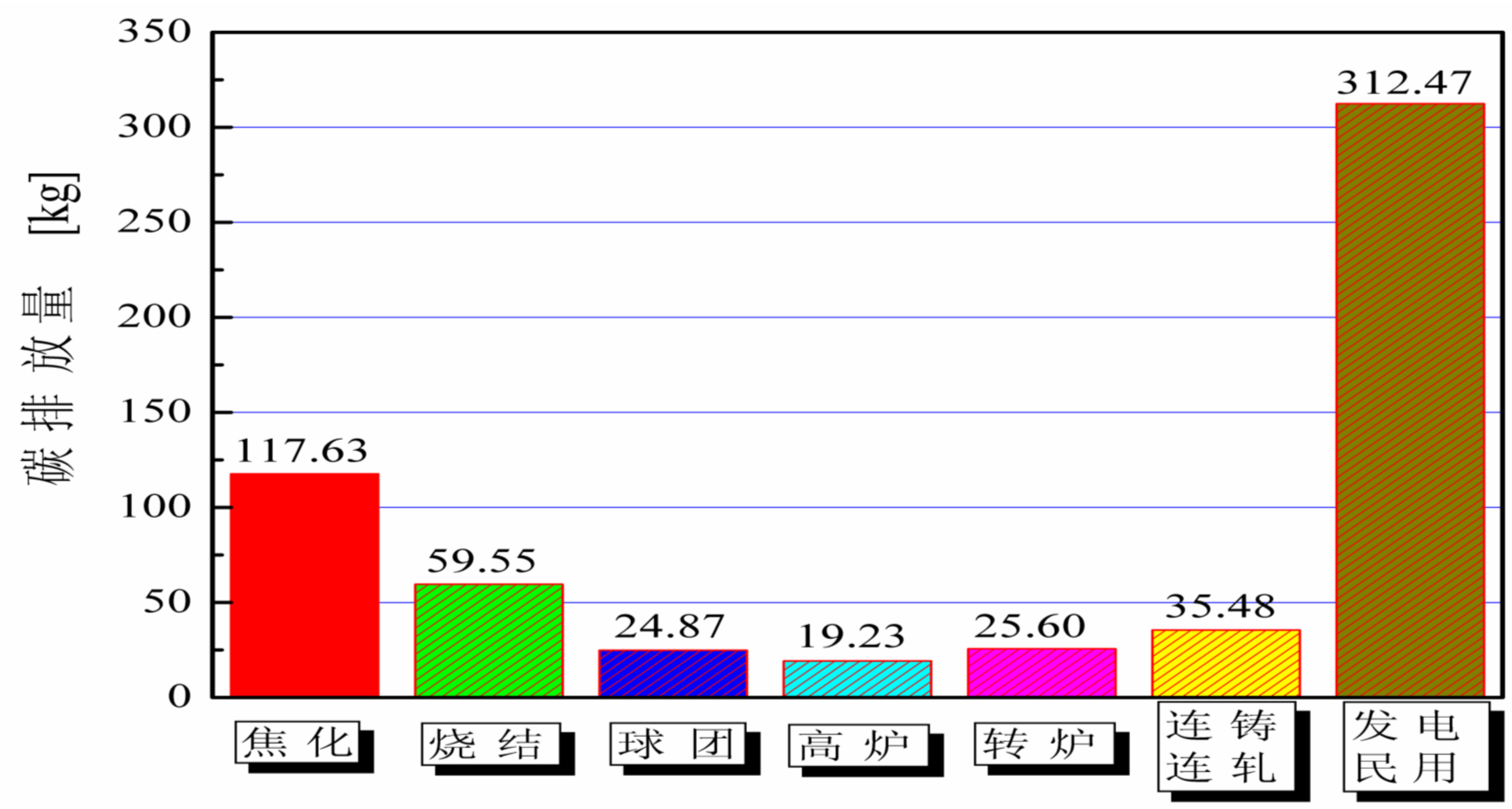
The main CO_2 emission unit in the long steel production process



高炉-转炉长流程钢铁生产过程是中国钢铁行业主流工艺/焦化、烧结、高炉、转炉、发电等单元是主要CO_2排放源

钢铁主要生产单元CO_2排放量

The CO_2 emissions of the main steel production units



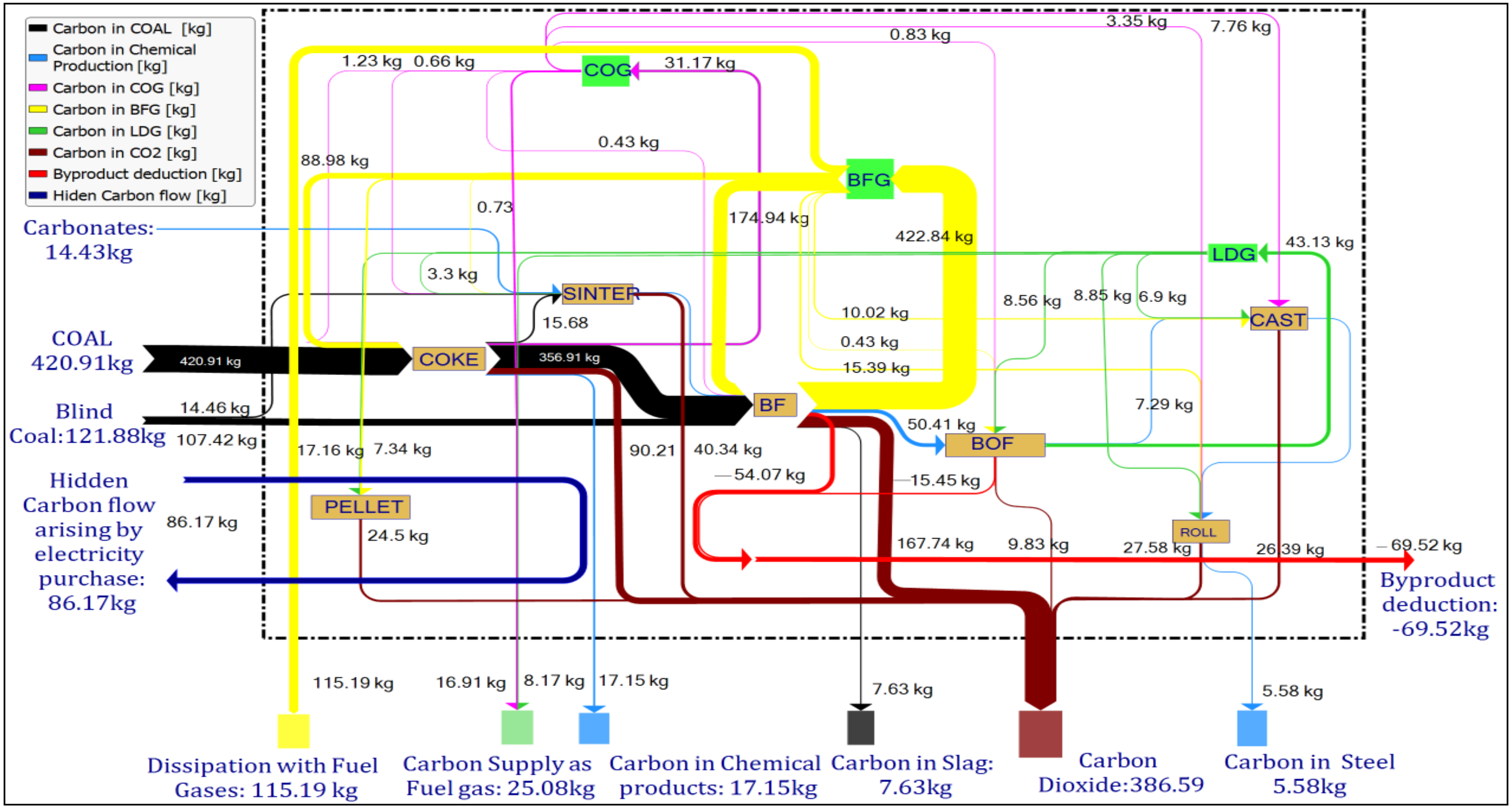
典型长流程钢铁生产过程单元碳排放（**kg/t**粗钢）

–中科院过程工程研究所技术报告

典型长流程钢铁企业碳物质流分析图

The flow diagram of carbon material in steel production process

构建了典型企业全过程碳物质流图/CO_2接排放量为1928.92 kgCO_2/吨粗钢



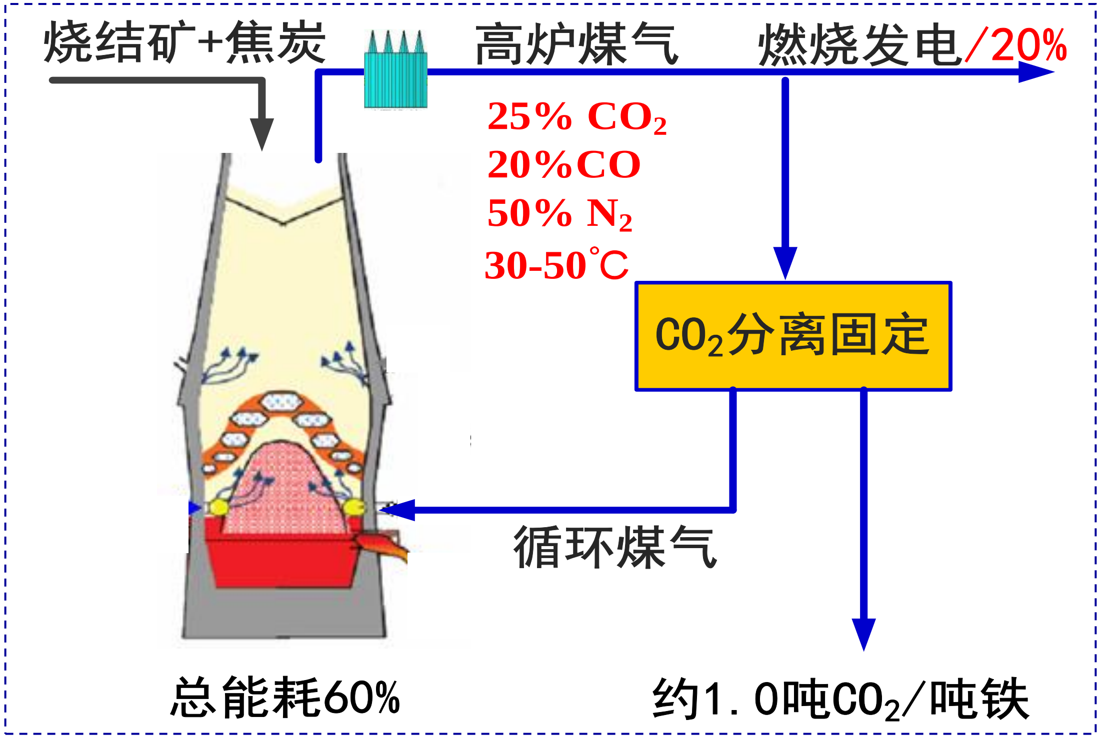
–Zhang H, Dong L, Li H Q, et al. Energy policy. 2013

钢铁工业过程低碳发展的CCUS机会

The CCUS opportunity of low carbon development process of steel industry

欧盟、日本、中国等均启动钢铁行业低碳行动创新计划。

The European Union, Japan, Chinese are all starting the low carbon innovation plan of iron&steel industry



预期实现钢铁CO_2减排30%以上

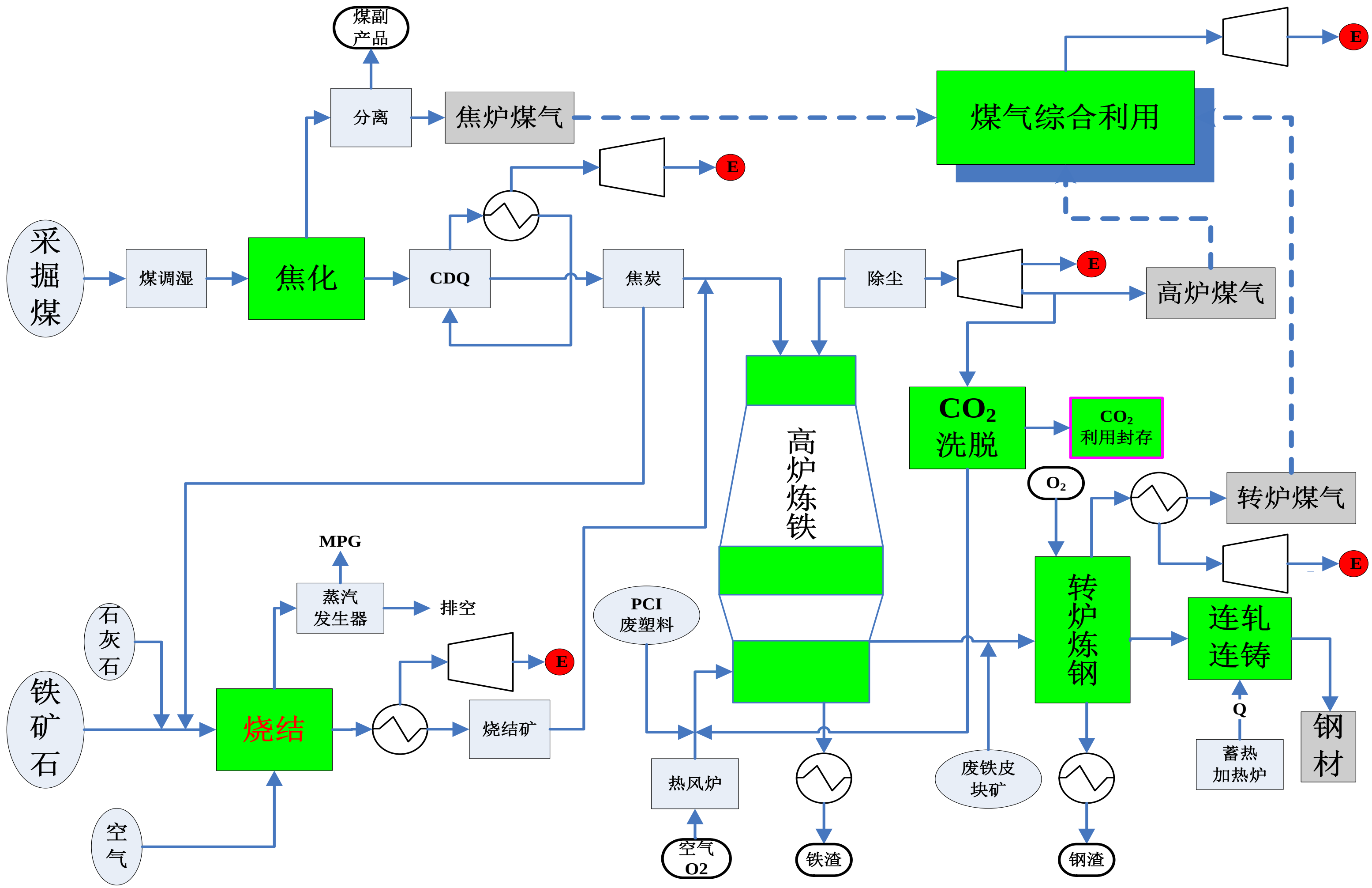
The steel CO_2 reduced by more than 30%

- ✓焦炉/高炉煤气提质利用与CCS结合；
- ✓熔融还原与CCS结合；

- ✓低成本的CO_2分离技术？
- ✓捕获的大量CO_2如何利用？
- ✓全系统层面如何分析评价CCUS潜力

中国典型钢铁生产流程CCUS应用技术思路

Typical steel production process and application of CCUS in China



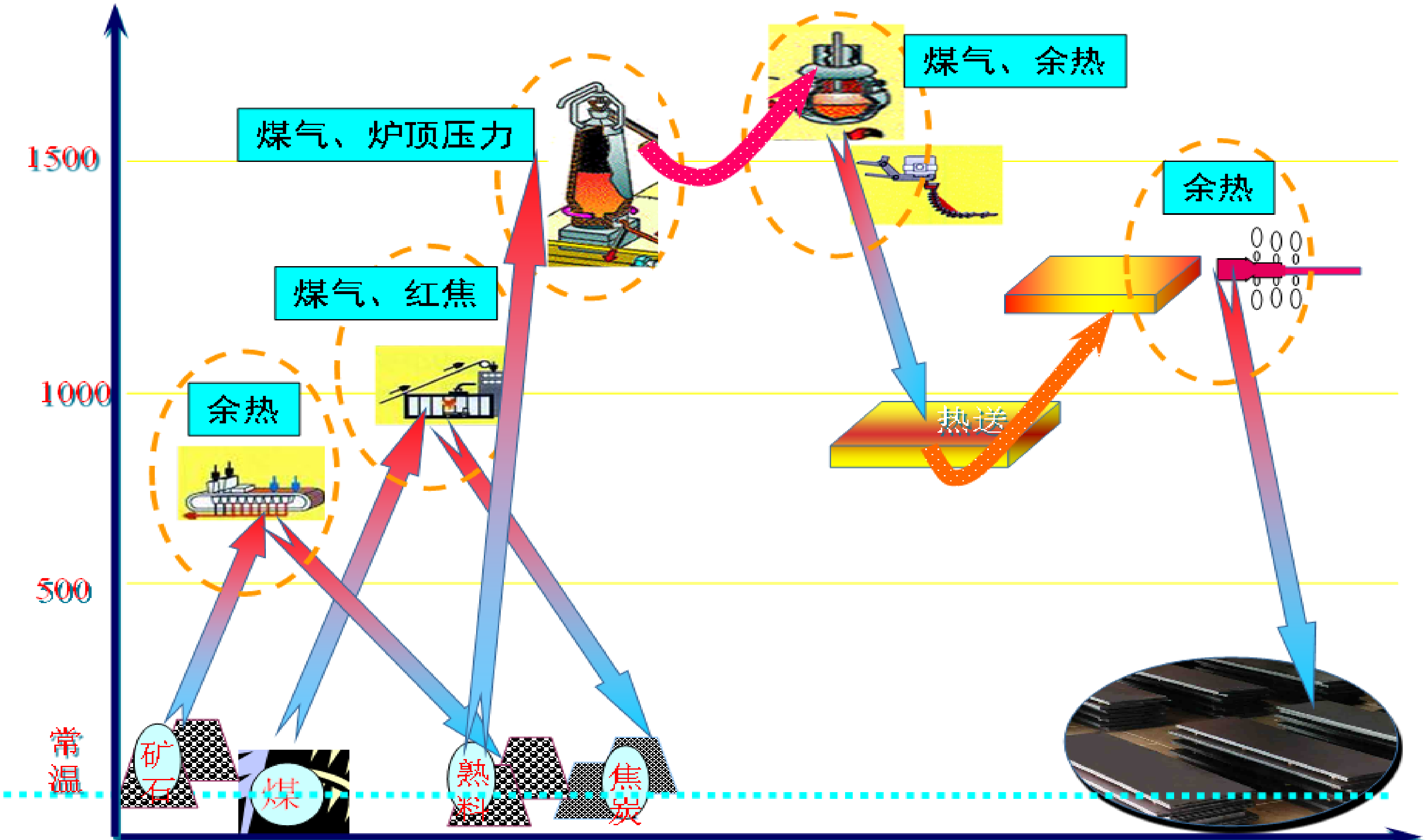
余能优化利用减排-高热值煤气化工利用-捕获CO_2碳酸化原位固定

–技术案例1：余能优化利用与CCUS 结合

Case1: The combination of CCUS and the utilization of waste heat

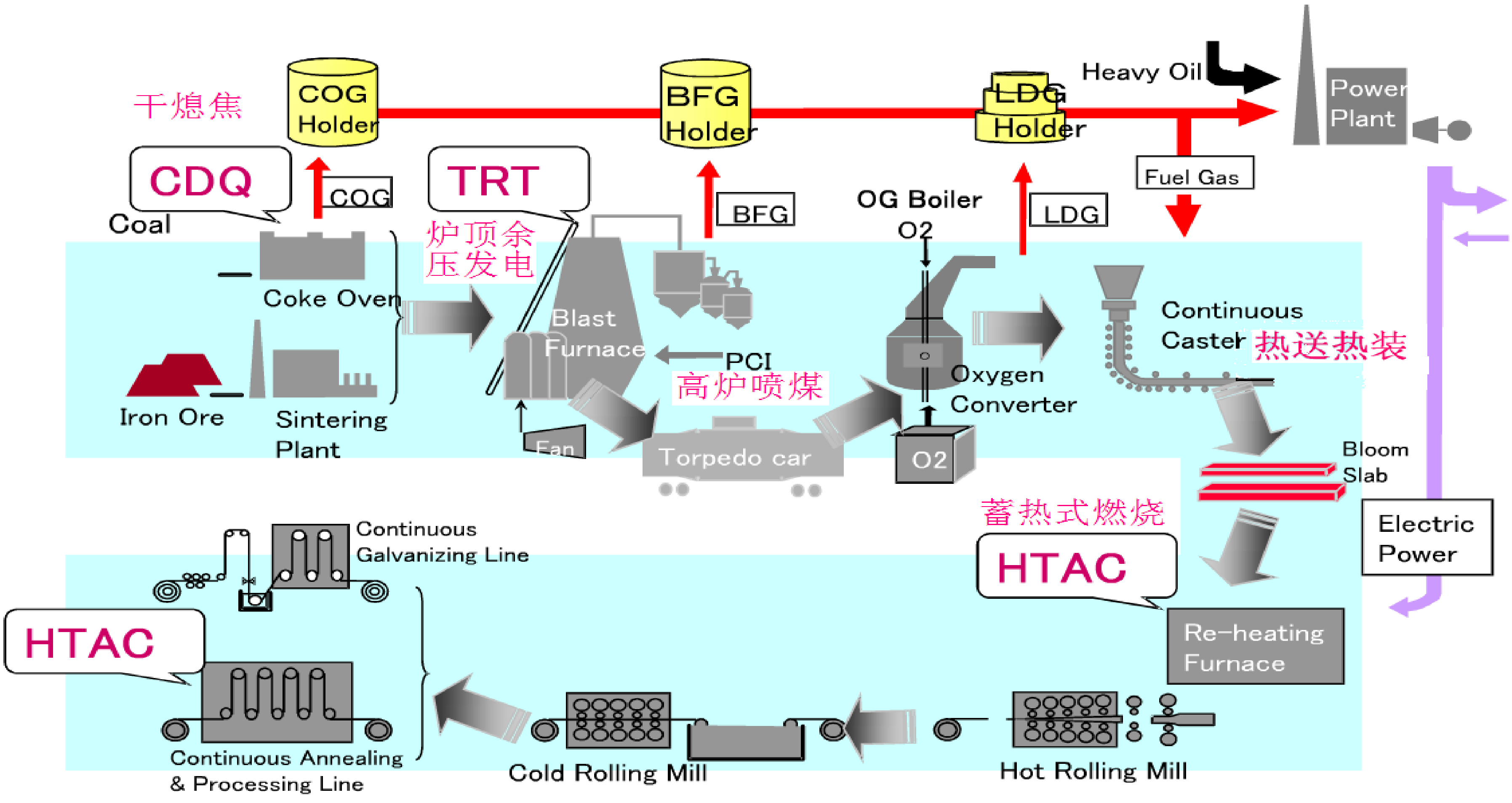
典型长流程钢铁生产过程能量流动

The energy flow in typical steel production process



余能回收集成网络CO_2减排潜力

The CO_2 mitigation potential in energy recovery network



最低实现10～30%的CO_2减排/增加CCUS过程将进一步提高减排潜力

尾气余能余热利用技术实际应用案例

The application case of exhaust energy utilization technology


烧结矿尾气余热回收发电系统

Sinter exhaust waste heat recovery and power generation system

转炉烟气回收发电系统

Converter gas recovery power generation system

✓每年减排CO_2 160万吨

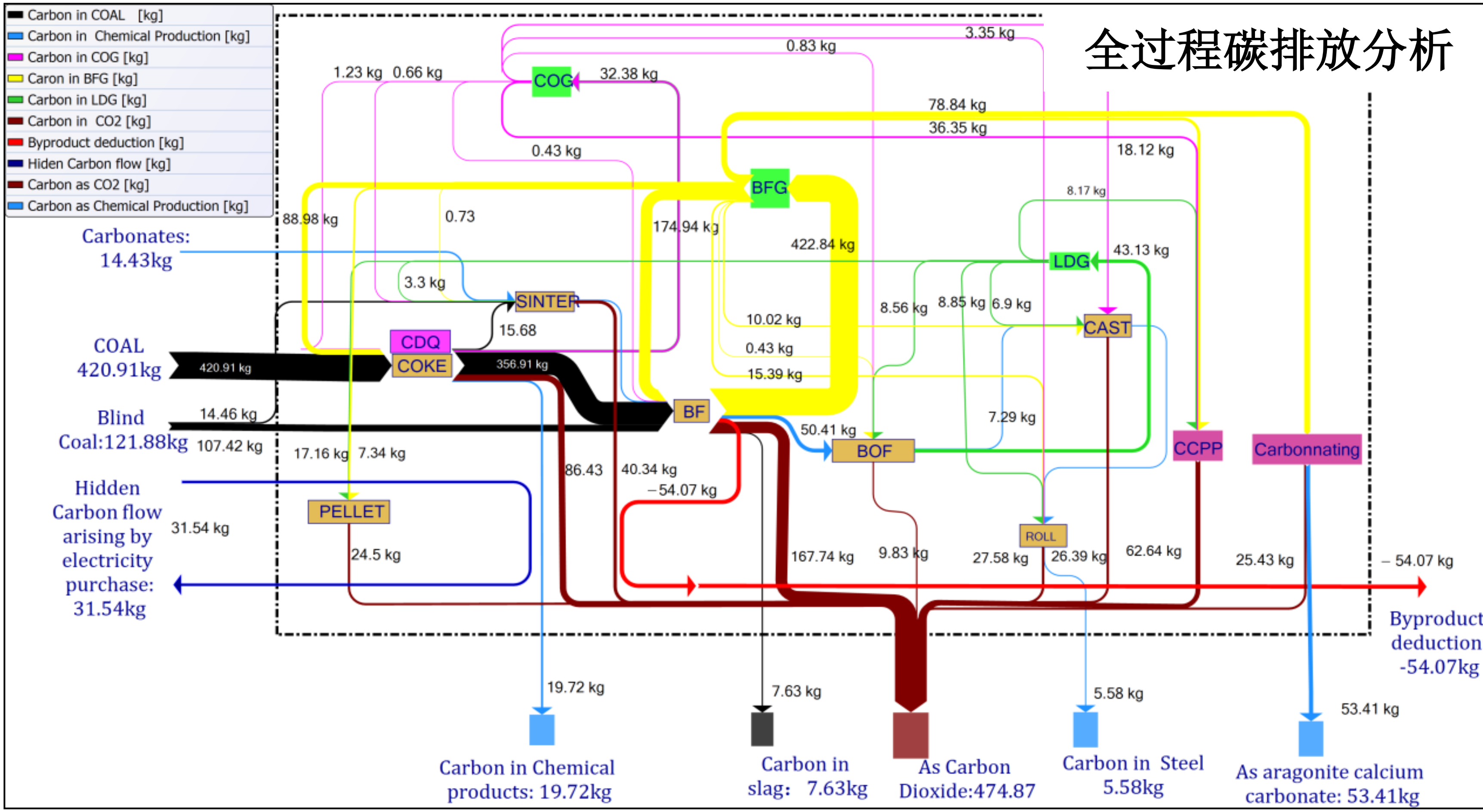
CO_2 annual emission reduced by 16 million tons

✓中国第一个冶金过程CDM项目

Chinese first CDM project of metallurgical process

余能利用技术与CCUS技术结合碳排放情景分析

The carbon emission scenario analysis



过程CO_2排放估算为1671.92 kgCO_2/吨粗钢，相当于降低碳排放15%。

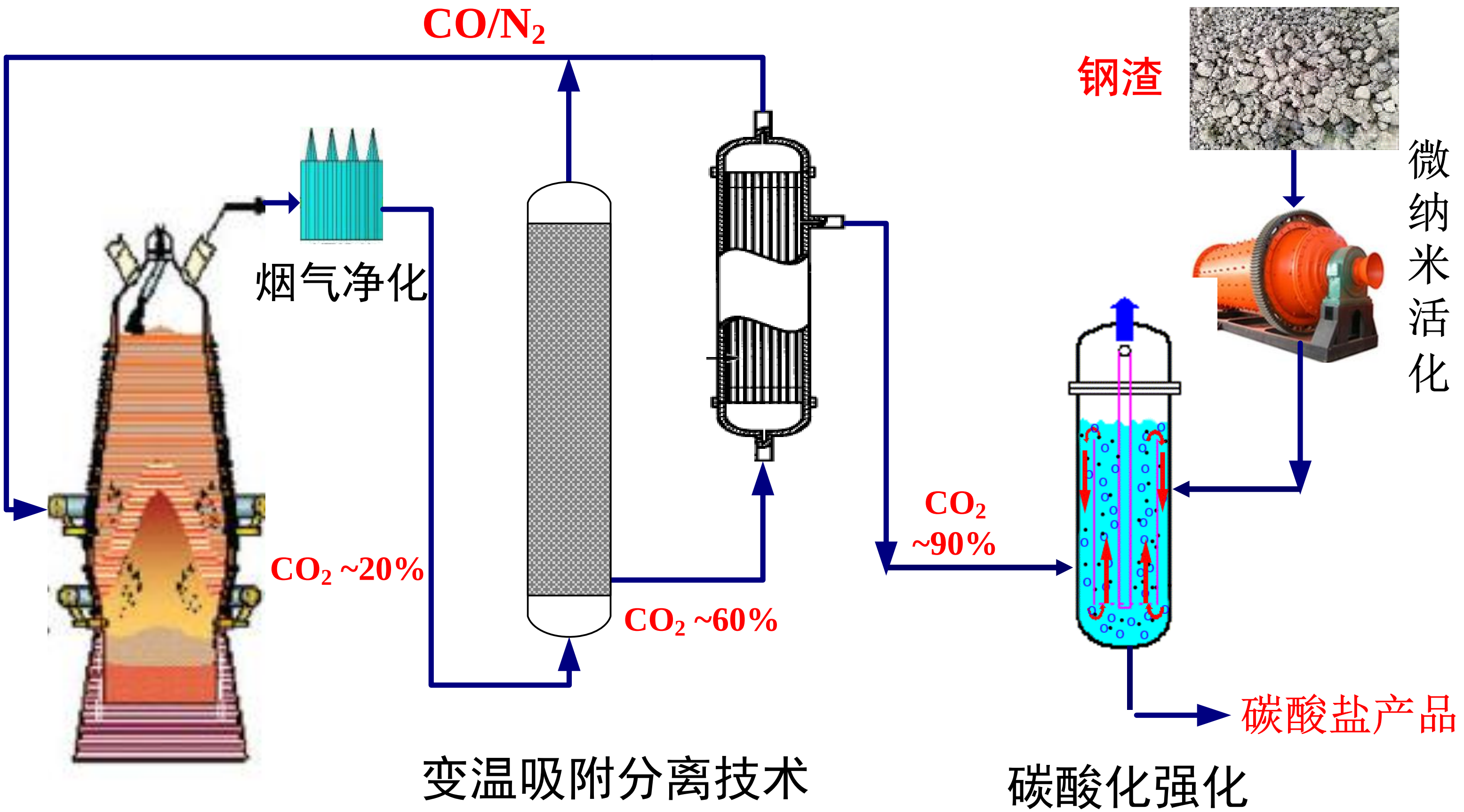
–Zhang H, Dong L, Li H Q, et al. Sustainable Energy Technologies and Assessments, 2013

技术案例2：捕获CO_2的碳酸化原位转化固定

Technique Cases 2: CO_2 Capture by Situ Carbonation and Fixation

CO_2低成本分离与钢渣碳酸化矿化固定

CO_2 Separation and Mineral Sequestration by Steelmaking Slag



钢铁过程余热强化变温吸附分离/CO_2钢渣钙基固废矿化固定

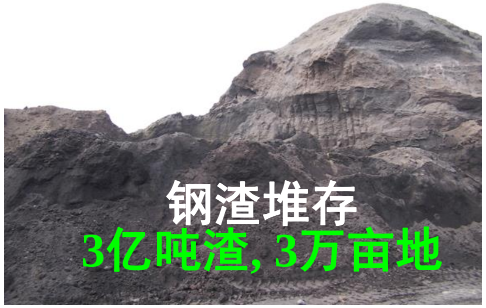
Strengthen TSA and separation of waste heat/CO_2 mineral sequestration by calcium based solid waste

钢渣是钢铁过程排放的难处理大宗固废

Steelmaking Slag is a kind of Solid Waste Produced by Steel Process

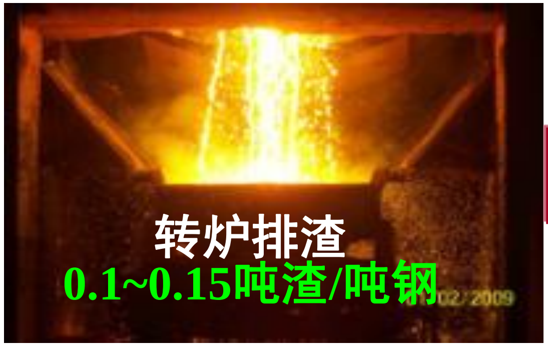
钢铁生产过程大量钢渣选铁尾渣没有有效利用，游离CaO和MgO遇水体积膨胀，存在安全风险

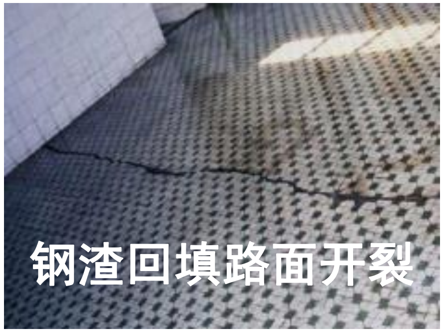
- 排放量大(large capacity of drainage)：年产量约7000万吨
- 资源浪费（resource waste）：利用率35%，累积堆存3亿吨



氧化钙体积膨胀率约200%： $CaO + H_2O \rightarrow Ca(OH)_2$

氧化镁体积膨胀率约77%： $MgO + H_2O \rightarrow Mg(OH)_2$

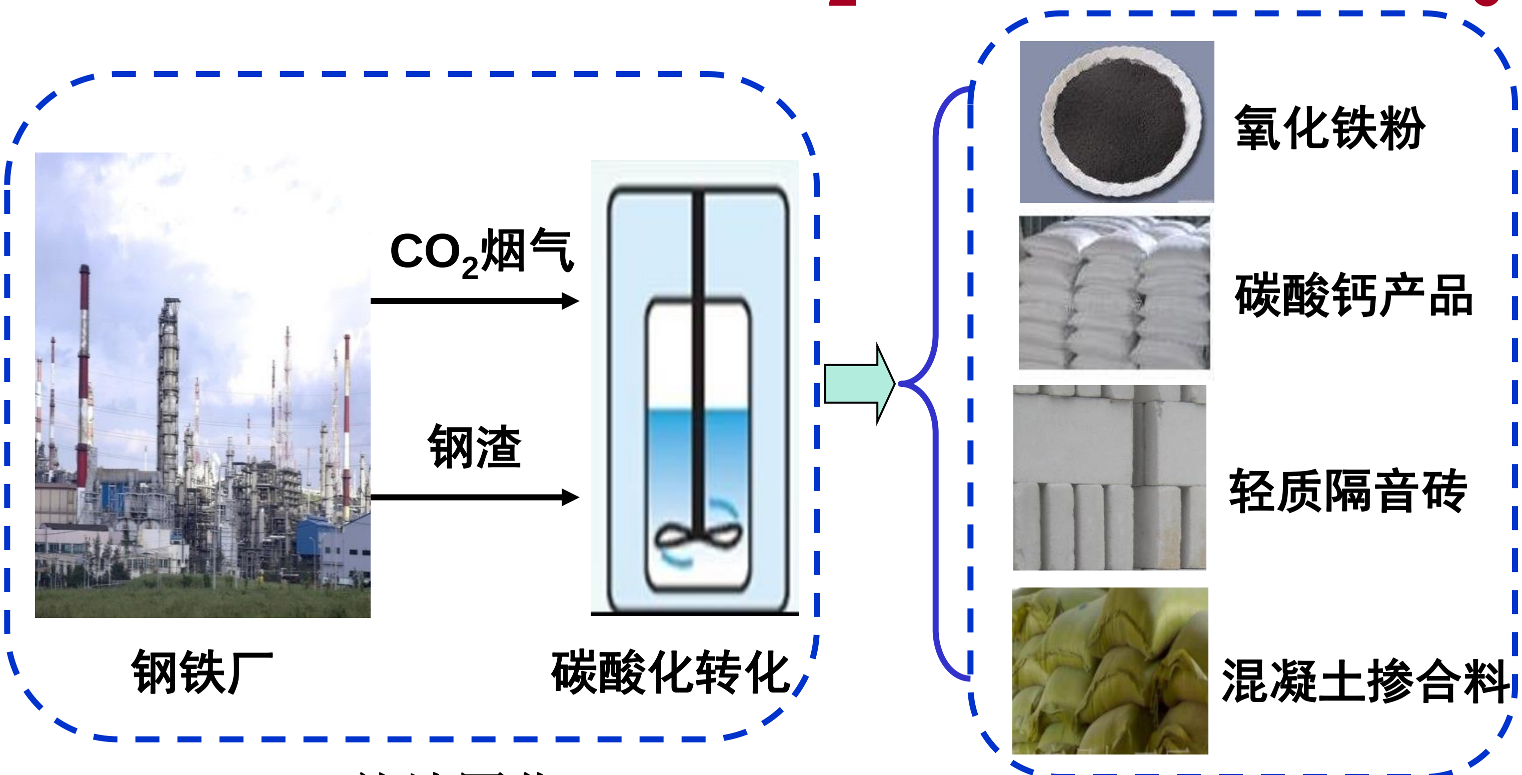




CO_2钢渣碳酸化矿化固定

CO_2 Mineral Sequestration by Steel Slag Carbonation

Ca/Mg基矿物 + CO_2 → (Mg, Ca)CO_3



CO_2就地固化

CO_2 situ fixation

多组份高值化利用

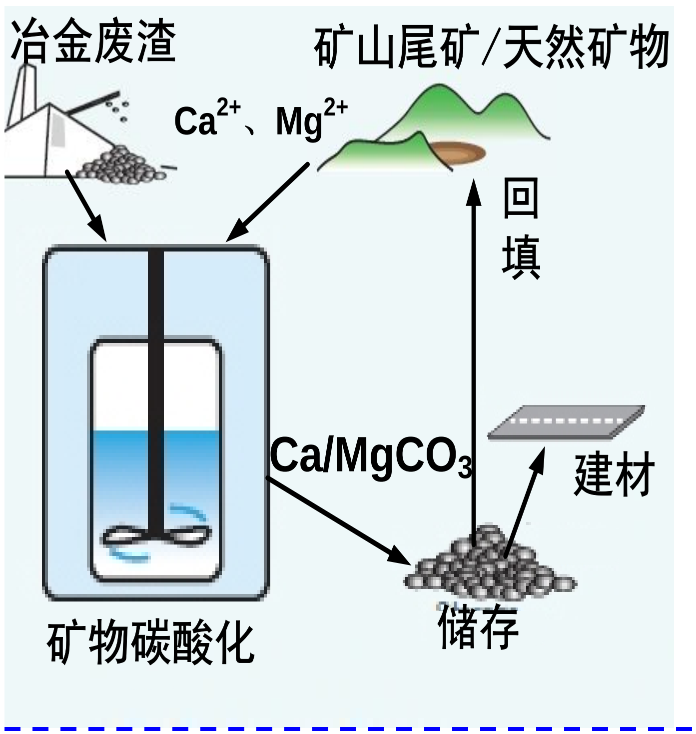
High value application of multicomponent

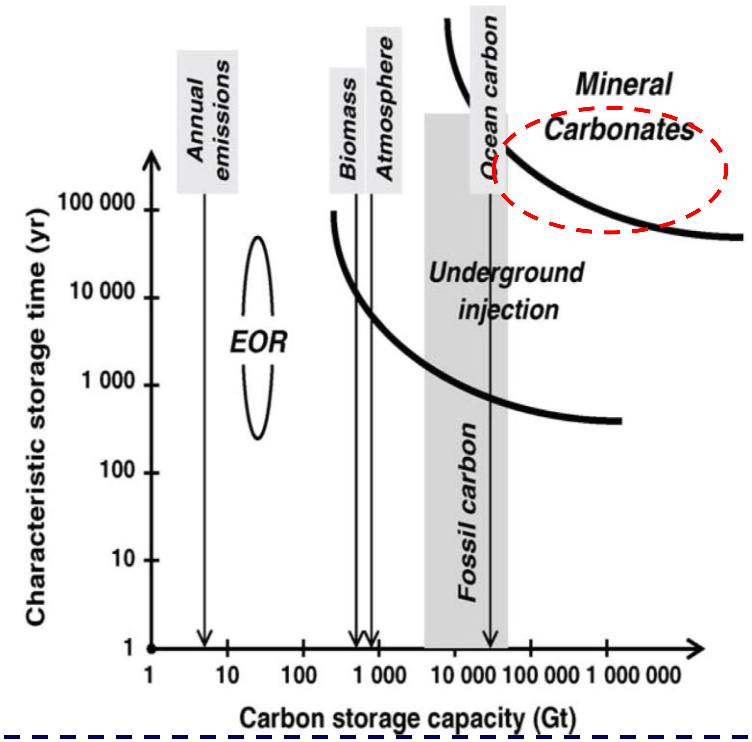
实现钢渣和CO_2协同利用，以废治废，实现原位固碳。

CO_2矿化固定是CCUS研究热点

CO_2 Mineral Sequestration is a CCUS research hotspot

90%CO_2





R.Zevenhoven et al.,Greenhouse Gases: Sci. & Tech. 2011,1,45

K. S. Lackner. Science 2003,300,1677

- 存储容量大，可实现原位固定
- 存储物长时间安全、稳定，对环境影响较小
- 具有较低的投资成本与运行成本，容易与其它工业过程集成

CO_2 矿物固定原料

Materials for CO_2 mineral sequestration

Ca/Mg基矿物可作为CO_2矿物固定的原料/Both Ca/Mg-based minerals and industrial solid residua can be used as raw materials for CO_2 mineral sequestration.

	矿物	组成/Composition		Rc, kg/kg	R_{CO2}, kg/kg
		MgO, wt%	CaO, wt%		
minerals: Peridodites	Dunite (纯橄榄石)	49.5	0.3	6.8	1.8
minerals: Peridodites	Harzburgite(斜辉橄榄石)	45.4	0.7	7.3	2
minerals	Serpentinite（蛇纹石）	～40	～0	～8.4	～2.3
minerals	Wollastonite（硅灰石）	-	35	13	3.6
solid residua	Talc	44	-	7.6	2.1
solid residua	Iron & steelmaking slag	～10	40～65	～7	～1.9
solid residua	Municipal solid waste incinerator	-	20～35	～17	～4.6
solid residua	Waste concrete and cement	-	10～30	～23	～6.4
	Cement kiln dust	1-2	46～50	～8.4	～2.5

- ✓ **总体碱性/富钙；Generally alkaline and rich in calcium;**
- ✓ **低成本；易工业化；比原生矿更具化学不稳定性；Their low costs, the widespread availability in industrial areas and their chemical instability shown more reactive than primary minerals;**
- ✓ **金属元素含量丰富，可回收并工业化应用；Contain abundant metal elements, which can be recovered for further industrial application.**

固体残渣碳化封存CO_2

CO_2 sequestration by solid residua carbonation

- 利用固体废弃物作为CO_2固化原料具有巨大市场潜力；**The breakthrough concept of using solid residua as raw materials for CO_2 sequestration have great potential market, especially for the development of Circular Economy in China.**

过程工业名称 Process industry	固体残渣生产& $CaCO_3$需求情况 Situation of solid residua production & $CaCO_3$ demand	
Iron & steel industry	Steelmaking slag > 50 Mt/y	Utilization ratio limited to about 40%
Cement factory	Cement kiln dust > above 60 Mt/y	Difficult to be used
Chemical industry	salt slurry: 1.3 Mt/y; boric sludge landfill > 17Mt	
$CaCO_3$ industry	High value-added $CaCO_3$ > 13 Mt/y; low value-added $CaCO_3$ > 5000 Mt/y	Be in hare demand

氧化钙含量很高，固体残渣可作为廉价原料的高附加值生产碳酸钙，以及间接CO_2矿物封存

迫切需要提高碳酸化固碳效率

urgent need to improve the efficiency of carbon fixation and carbonation

钢铁冶金渣
(年排放3亿吨)

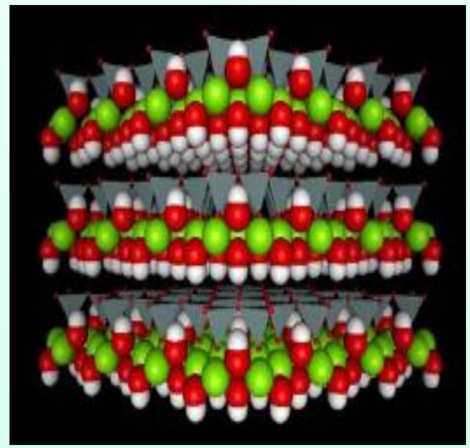
CaO ~45%

MgO ~10%

矿山尾矿
(年排放10亿吨)

MgO ~40%

CaO ~20%



钙镁硅基矿物
固碳活性组份反应

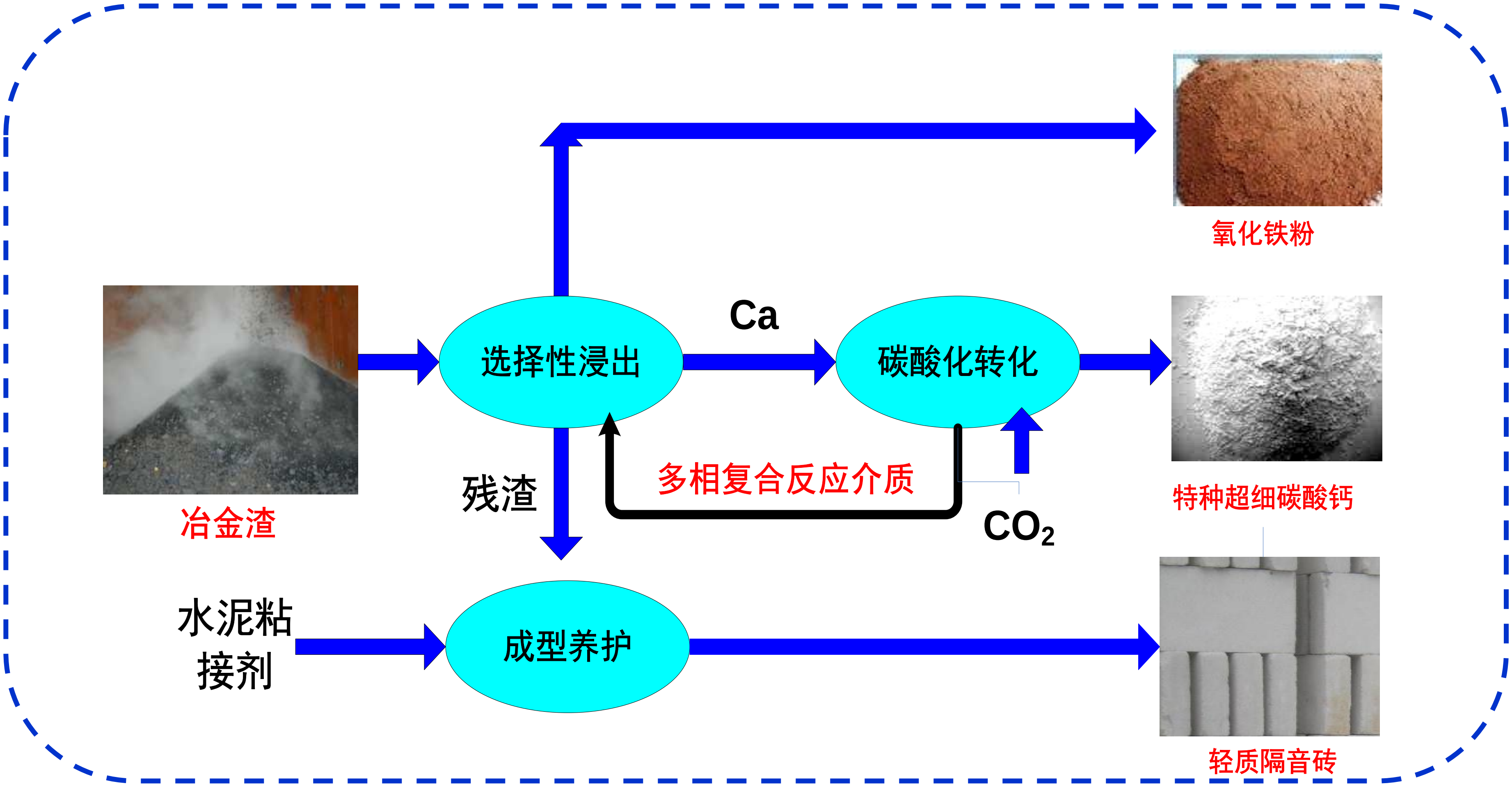
- ✓ 矿化反应缓慢钙
- ✓ 钙镁转化率20%
- ✓ 产物资源化利用难

J. Sun, Energy & Environmental Science, 2008, 1, 370

K. E. Kelly, J. Greenhouse Gas Control ,2011, 5, 1587

IPE：复合介质强化钙基固废矿化固定CO_2

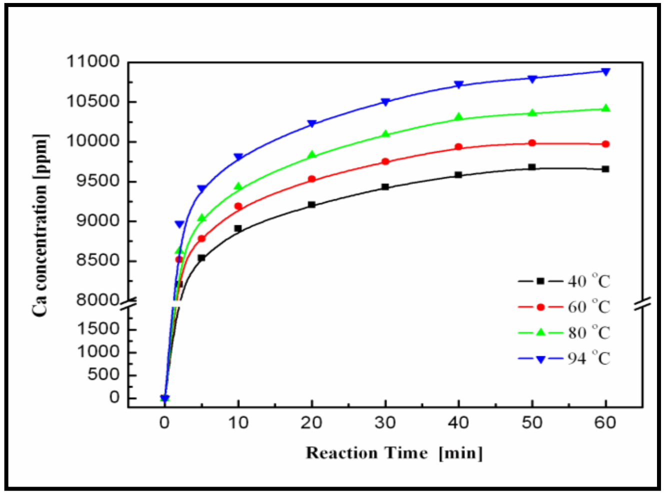
IPE：Composite medium fortified with calcium based solid mineralizing fixed CO_2



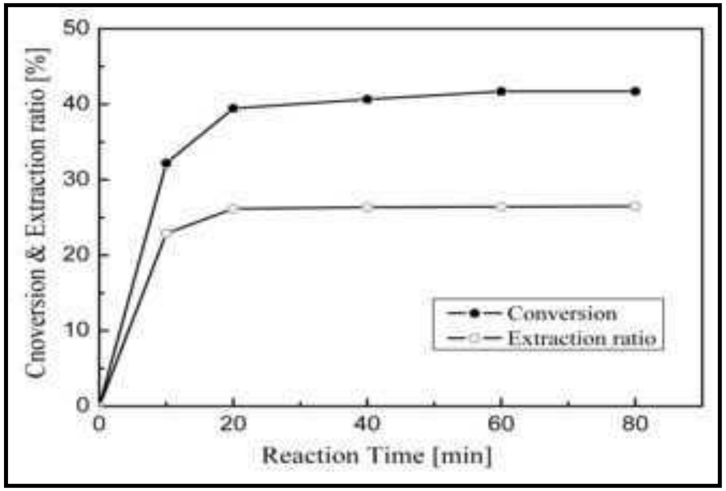
冶金渣CO_2碳酸化转化联产超细碳酸钙新工艺

碳酸化强化工艺特色

The carbonation process characteristics



钙/镁提取率大于70%



单程碳酸化转化率达到50%

生产超细文石型碳酸钙

多孔尾渣生产吸引砖等高端建材

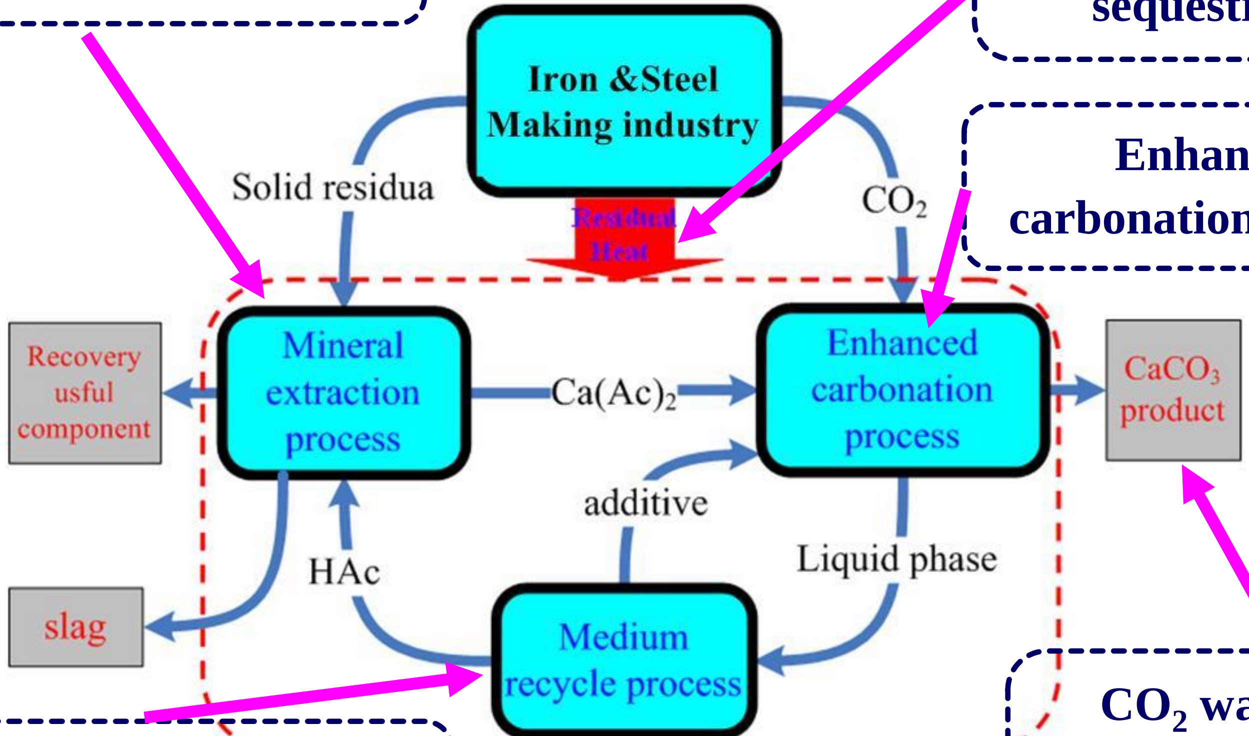
强化碳酸化矿化工艺在钢铁生产过程的应用

The carbonate mineral sequestration Technology applied in steel process

Selective leaching of metals from steelmaking slag

Waste heat can be integrated in CO_2 mineral sequestration rout

Enhancing CO_2 carbonation & conversion



Reaction medium completely and effectively recycling

CO_2 was effectively converted into value-added product

5000吨/年$CaCO_3$中试装置

5000 t/a pilot plant for $CaCO_3$ production

Minerals extraction process

Enhanced carboantion process

Heating system

Dry segment of $CaCO_3$

CO_2净固化效率比较

Comparison of net CO_2 sequestration efficiencies

Feedstock	Process route	Leaching media	η_{CO_2} [%]	Product utilization	reference
wollastonite	direct	water	68.74	landfill	
wollastonite	direct	water	61.74	landfill	
Steel slag	direct	water	55.74	landfill	
Olivine	direct	water	58.74	landfill	
serpentine	direct	water	68.74	landfill	
Mg-silicate	indirect	Molten MgCl2	56.74	$MgCO_3$	
Waste cement	indirect	water	66.74	$CaCO_3$ used for desulfurize	
wollastonite	indirect	Acetic acid	71.74	$CaCO_3$	
Mg-silicate	indirect	HCl	<0	$MgCO_3$	
limestone	direct	-	-36.32	Ground calcium carbonate	
limestone	indirect	water	-138.47	Precipitate calcium carbonate	
Steel slag	**indirect**	**TBP-HAc**	**202.01**	**Precipitate calcium carbonate**	**This work**

Product after CO_2 sequestration not valuable use

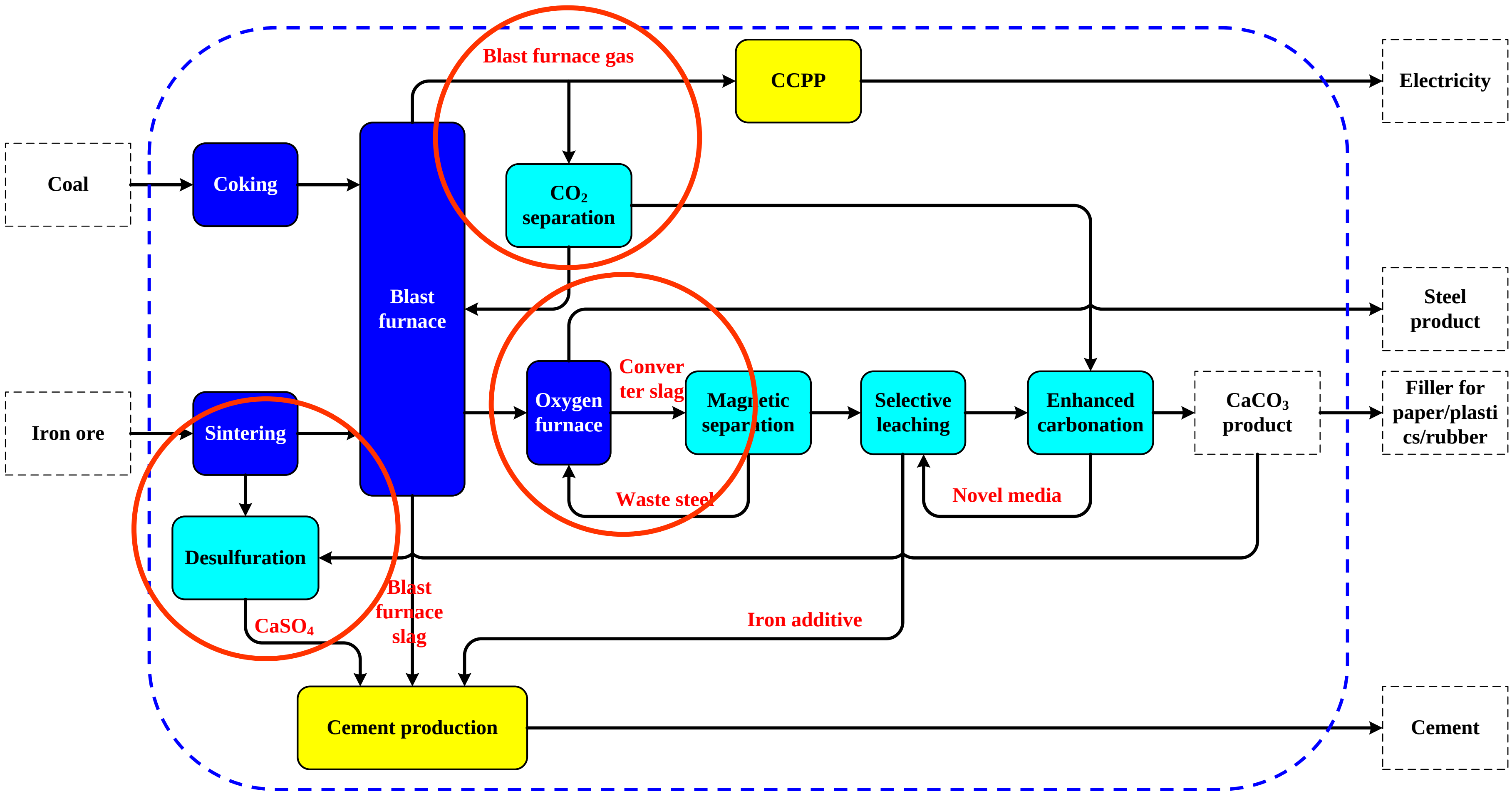
Bad industrial operability and low efficiency

Traditional $CaCO_3$ production emits large plenty of CO_2

Reaction media effectively recycled, product has high value

About 0.9 ton CO_2 could be reduced per ton precipitated $CaCO_3$ production.

生态系统集成新工艺
Novel process integrated Eco-System



- CO_2 comes from blast furnace gas/CO_2 sequestration materials comes from steelmaking slag;
- $CaCO_3$ product used for sinter flue gas desulfuration;After CO_2 sequestration, all of the products used for cement production.

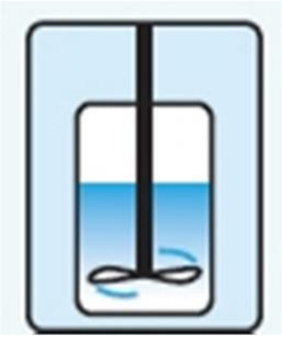
碳酸化矿化固定的减排潜力分析与拓展

The CO_2 reduction potential of mineral sequestration

钢渣碳酸化矿化固定CO_2减排潜力分析

钢渣矿化CO_2技术	单位减排量分析（吨／吨产品）		中长期减排潜力（万吨）	
	直接利用	综合减排	2020年	2030年
钢渣直接矿化CO_2技术	0.25	1.1	约500	约1500
钢渣间接矿化CO_2技术	0.27	1.26	10	240

碳酸化技术拓展



碳酸化技术

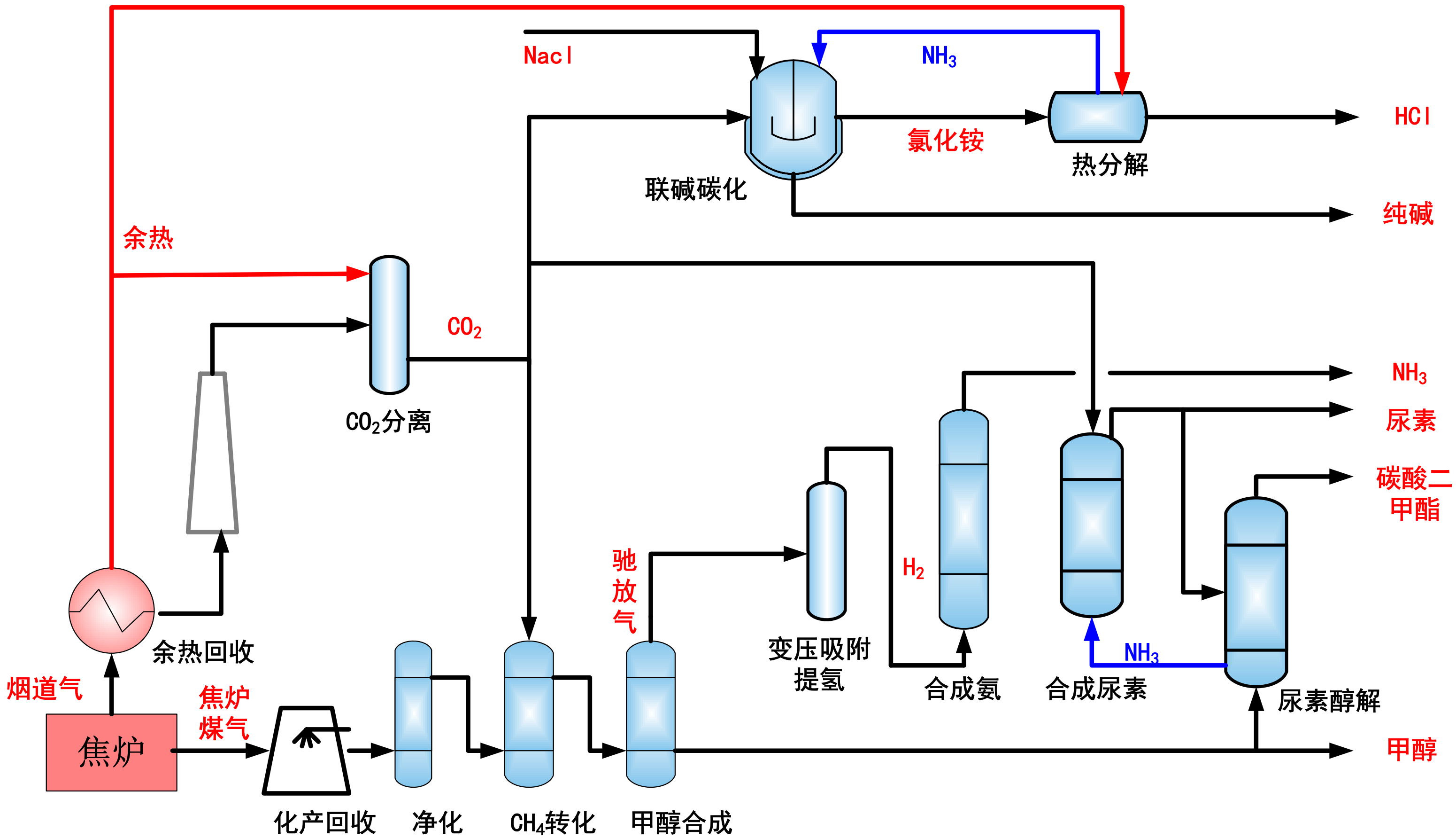
- ✓ 氧化铝行业：赤泥碳酸化
- ✓ 磷化工行业：磷石膏碳酸化
- ✓ 采矿行业：尾矿碳酸化
- ✓ 。。。。

技术案例3：焦炉煤气提质利用与CO_2化工利用结合

Case 3: Chemicals production from coke oven gas combined with CO_2 Recycling

焦炉煤气生产化工品与CO_2循环利用结合

Chemical production from COG combined with CO_2 utilization



焦炉煤气生产甲醇、合成氨以及下游尿素、碳酸酯等化工品；分离CO_2用于甲醇生产过程补碳、合成尿素与纯碱生产

Methanol, ammonia, urea and carbonate is produced from coke oven gas. CO_2 is utilized for carbon complement to methanol synthesis, urea and soda production

产业实施案例
Implementation case in industry

10万吨焦炉煤气生产甲醇装置

equipment of 100kt/a CH_3OH production from COG

5万吨甲醇驰放气联产合成氨装置

equipment of 50kt/a NH_3 production from methanol exhausted gas

	Regular ammonia routine	BFG routine
Hard coal（tce/t）	0.57	0
Soft coal（tce/t）	0.57	0
Electricity（tce/t）	0.11	0.28
Steam (t/t)	-0.37	3.19
Synthesis ammonia	52.01	35.04

冶金烟气中67.47%的碳元素以产品形态固定

67.47% of carbon element in flue gas is solidified in product

总结/Summary

- CCUS在钢铁生产过程具有巨大应用潜力/需要开展全过程系统分析与集成评估

  There is huge potential of CCUS applied on iron and steel industry and the systematic analylis and evaluation of the integrated process

- CO_2低成本分离与规模化利用是关键所在

  Low cost CO_2 separation and large-scale utilization is the key point

- 碳酸化原位固定与化工利用技术是重要发展方向

  CO_2 solidification through carbonation and chemical utilization is an important and effective route

–THANK YOU FOR YOUR ATTENTSION