



Excursus... Network Italiano SOFC

Una banca dati per lanciare la ricerca

Dr. Ing. Stephen McPhail – ENEA

Le celle a combustibile e l'idrogeno in Italia

Roma, 13 dicembre 2011

stephen.mcphail@enea.it

Excursus... Italian SOFC players



Companies



Universities



Tor Vergata (Rome)



Polytechnic of Turin



University of Perugia



University of Udine

Research Centres



CNR-IENI (Padua)



CNR-ISTEC (Faenza)



CNR-ITAE (Messina)



Edison (Milan)



Italian National Agency for New Technologies, Energy and Sustainable Economic Development

ENEA (Rome)



FN (Turin)

Excursus... Aree di interesse



➤ Synthesis & component manufacture

- Combustion synthesis: PoliTO
- Ball milling, jet milling: ENEA
- Wet chemistry, sol-gel: CNR-IENI, Tor Vergata
- Spark Plasma, P-Assisted Fast Electric Sintering: PoliTO
- Tape-casting: CNR-ISTEC, FN
- Extrusion: FN

➤ Deposition

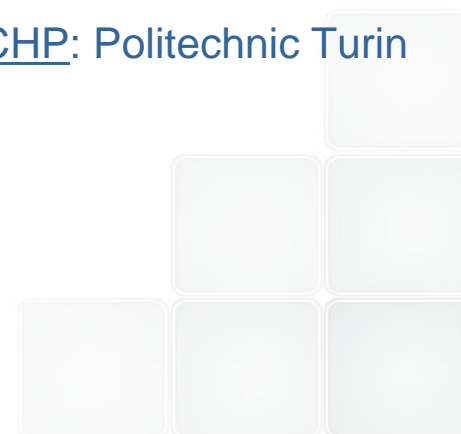
- Spray coating: CNR-IENI, CNR-ITAE
- Spin coating: Tor Vergata
- Magnetron sputtering: CNR-IENI, PoliTO
- Screen/stencil printing: CNR-ISTEC
- EBD: CNR-ITAE
- PVD (TC-PVD, EB-PVD): Edison, PoliTO
- PLD, EPD: Tor Vergata

➤ Cell & stack testing & characterization

- Comparative cell testing: Uni Perugia, ENEA
- Alternative fuels: CNR-ITAE, Edison, PoliTO

➤ System integration & testing

- SOFC modules: Edison
- Hybrid systems: CNR-ITAE
- Micro-CHP: Uni Perugia, ENEA, Politechnic Turin
- Sustainable CCHP: Politechnic Turin



Excursus... La proposta



Creazione di una **piattaforma sul web** (host: ENEA) dove **si profilano tutti i players Italiani** nel campo della ricerca & sviluppo sulle **SOFC**

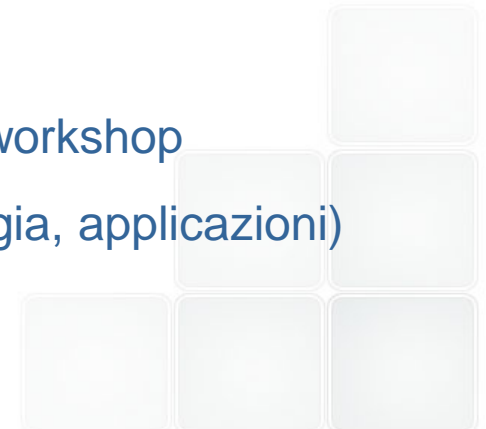
Visione: Promuovere la **coordinazione di ricerca, sviluppo e commercializzazione di SOFC** in Italia e facilitare lo sviluppo di prodotti al servizio del mercato mondiale

Ogni contribuente presenterebbe:

- Scheda con presentazione del laboratorio (ubicazione, strumentazione, nr. personale, finalità tecnico-scientifiche, ...)
- Scheda con attività in corso (programmi, partner, obiettivi tecnico-scientifici)
- Posizioni vacanti, borse di studio, dottorati, stage, scambi di personale, ...

Informazioni generali:

- Bandi emessi in corso, annunci di corsi, conferenze e workshop
- Scheda con descrizione generale delle SOFC (tecnologia, applicazioni)
- ...



Excursus... La proposta



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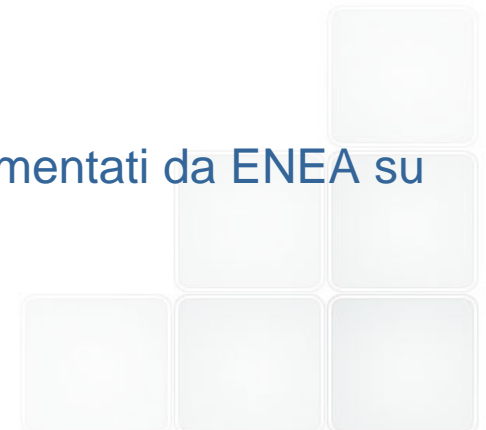
Esempio/modello: SOFC Canada (SOFCC Network, <http://www.sofccanada.com>)

- 21 gruppi di ricerca da 12 istituti
- Finanziato da NSERC e industria
- Finanziamento devoluto principalmente a formazione studenti
- 4 topic tecnici

Per adesso, in Italia: Un **sito statico**, con **aggiornamenti** implementati da ENEA su **segnalazione di partner** interessati. **Costi – 0€**

Futuro: area riservata per scambio di documenti?

Patrocinio H2-IT?





Le celle a combustibile nella catena *WASTE-TO-ENERGY*

Rovesciare il paradigma dei rifiuti

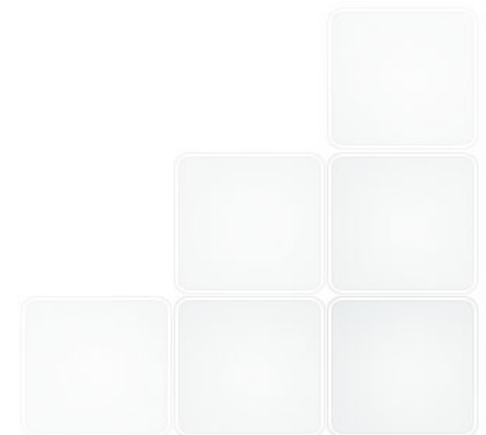
Dr. Ing. Stephen McPhail – ENEA

Le celle a combustibile e l'idrogeno in Italia

Roma, 13 dicembre 2011

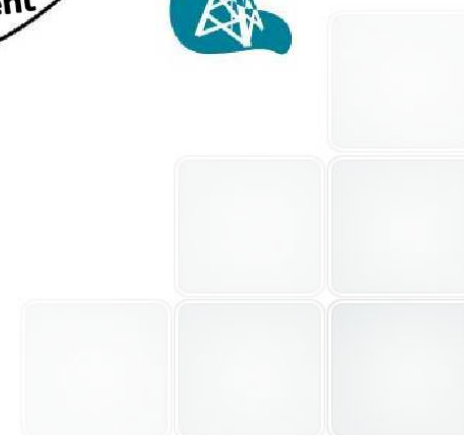
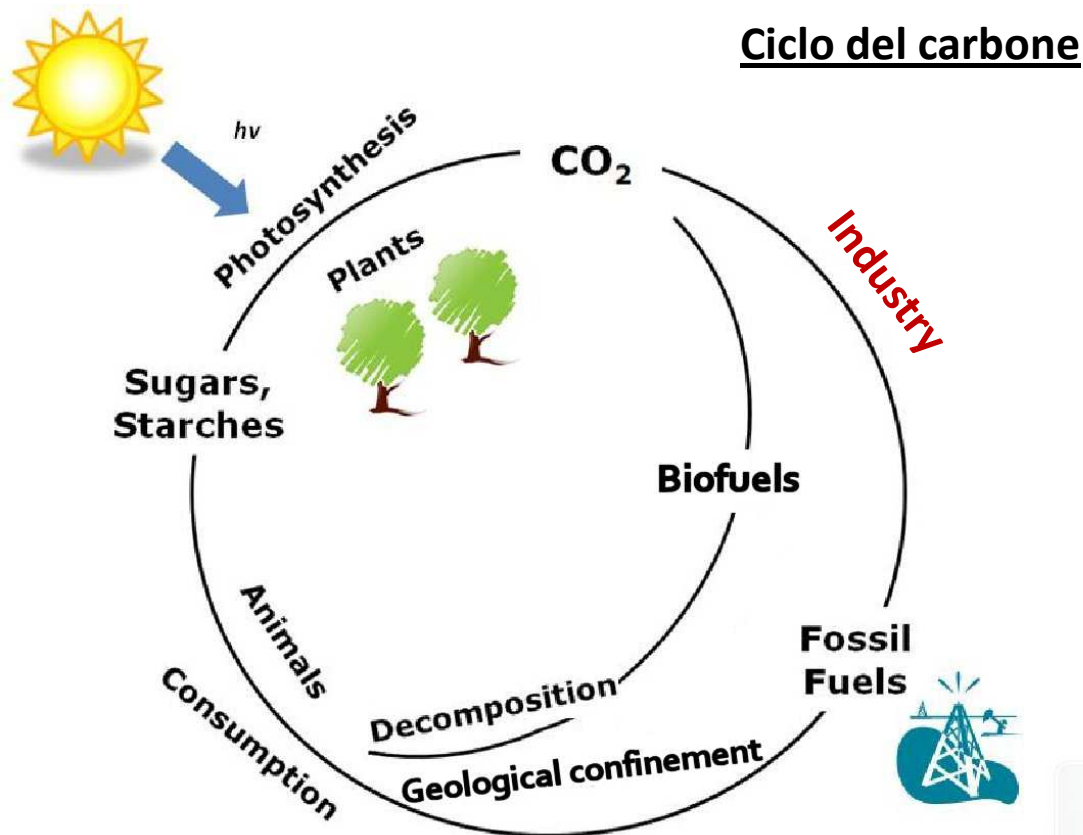
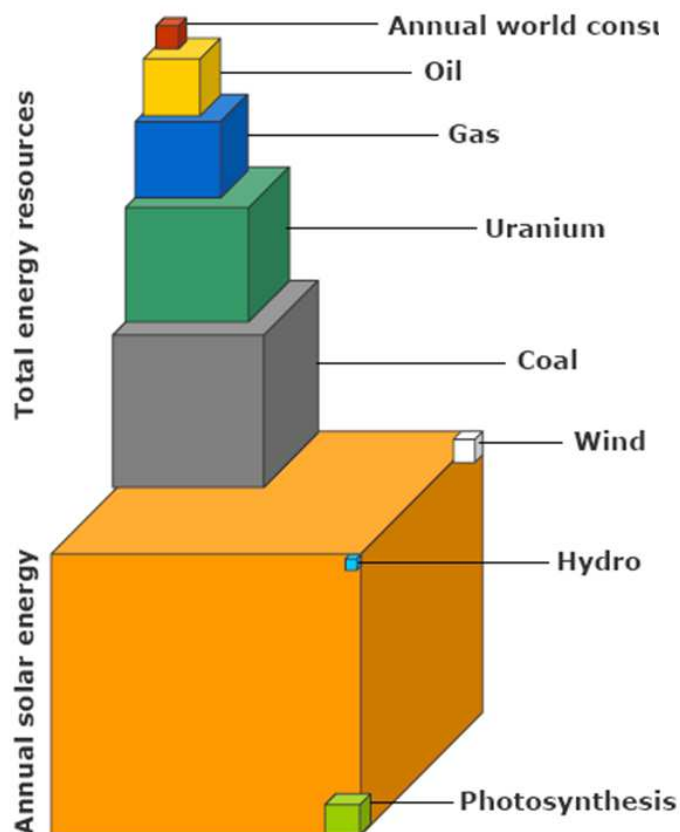
stephen.mcphail@enea.it

- La potenzialità energetica dei rifiuti
- Generazione distribuita
- Sistema-tipo
- Biogas: Clean-up
- Biogas: Uso in celle a carbonati fusi
- MCFC: anodi alternativi



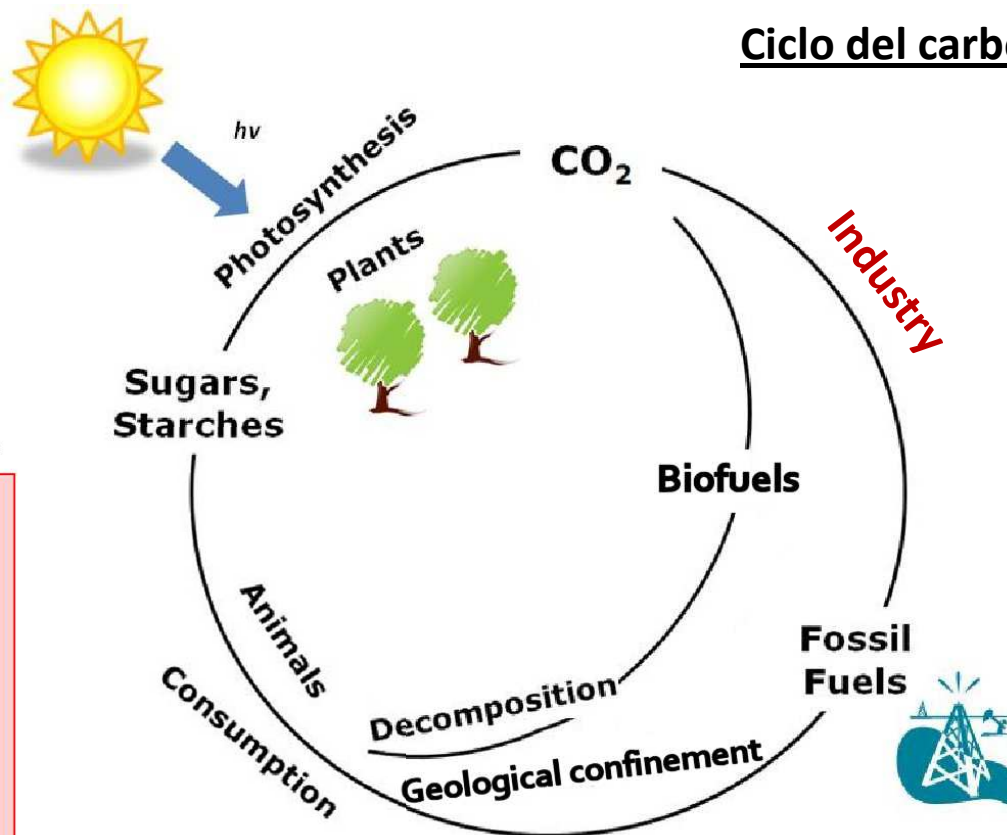
La potenzialità energetica dei rifiuti

Energia primaria

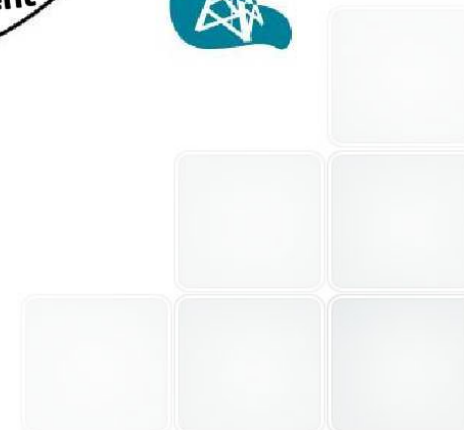
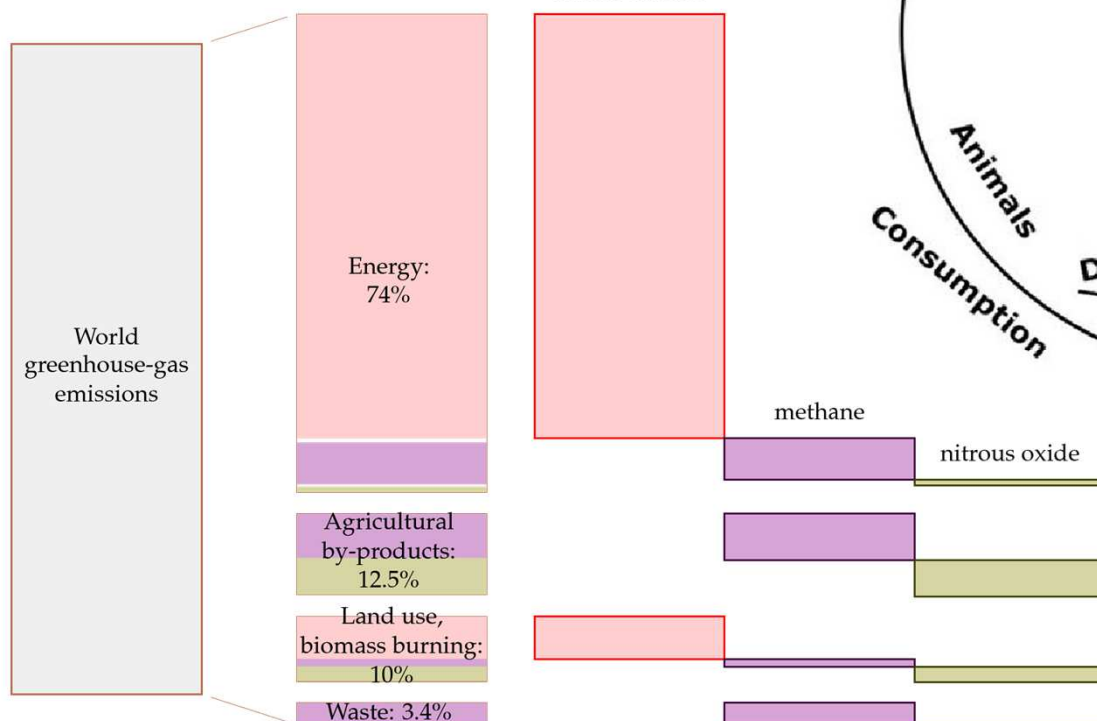


La potenzialità energetica dei rifiuti

Ciclo del carbone



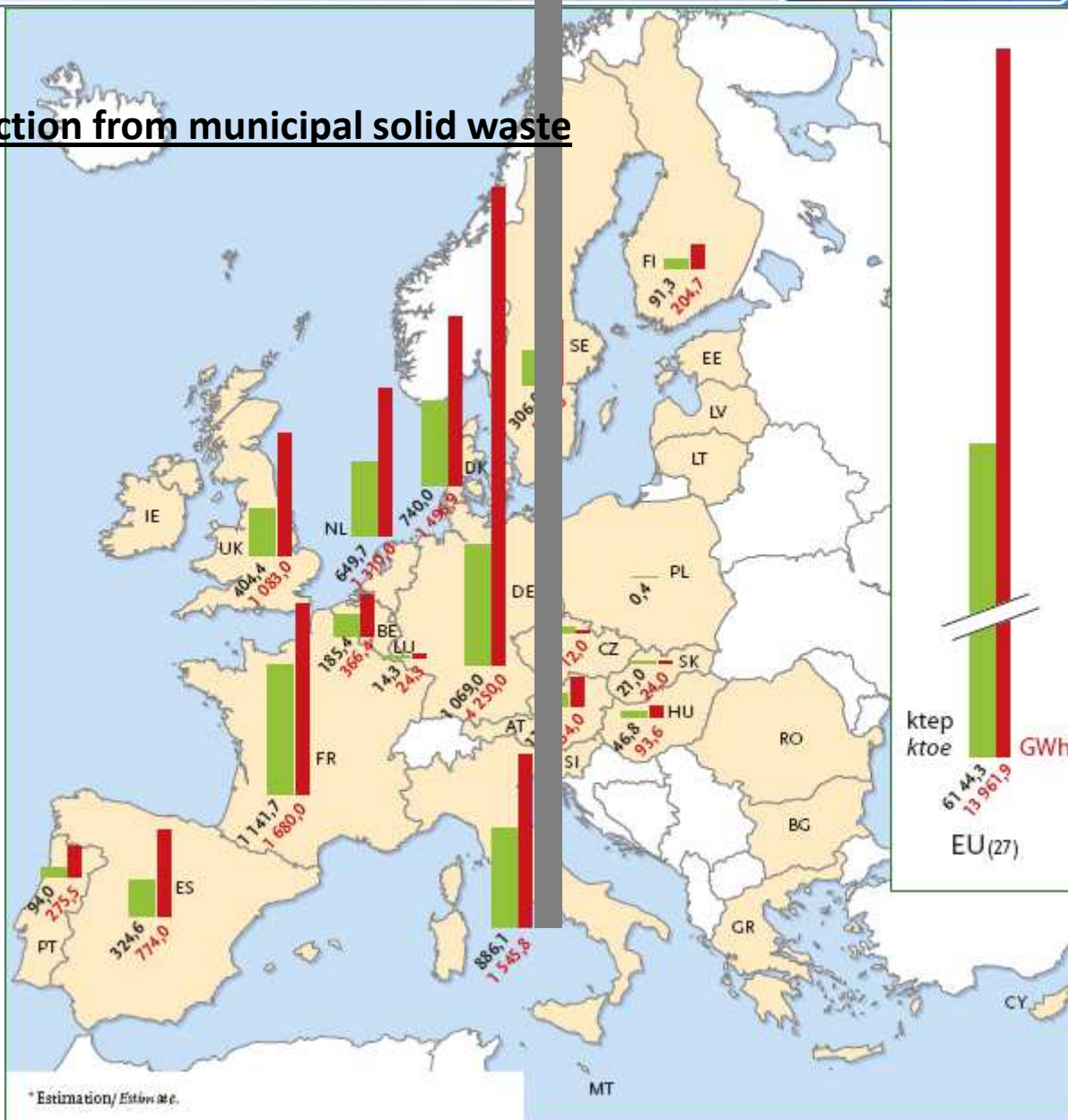
Emissioni gas serra



La potenzialità energetica dei rifiuti

Primary energy & electricity production from municipal solid waste

Produzione in Italia (2009):
 180 Mtep energia primaria
 18 Mtep da rinnovabili (inc. idro)
 0.9 Mtep energia da rifiuti (RSU)



La potenzialità energetica dei rifiuti



Biogas potential in Italy (2006)

Da FORSU:

$1.3 \times 10^9 \text{ m}^3$

= 620 ktep potere calorifico

Da allevamenti (bovini & suini):

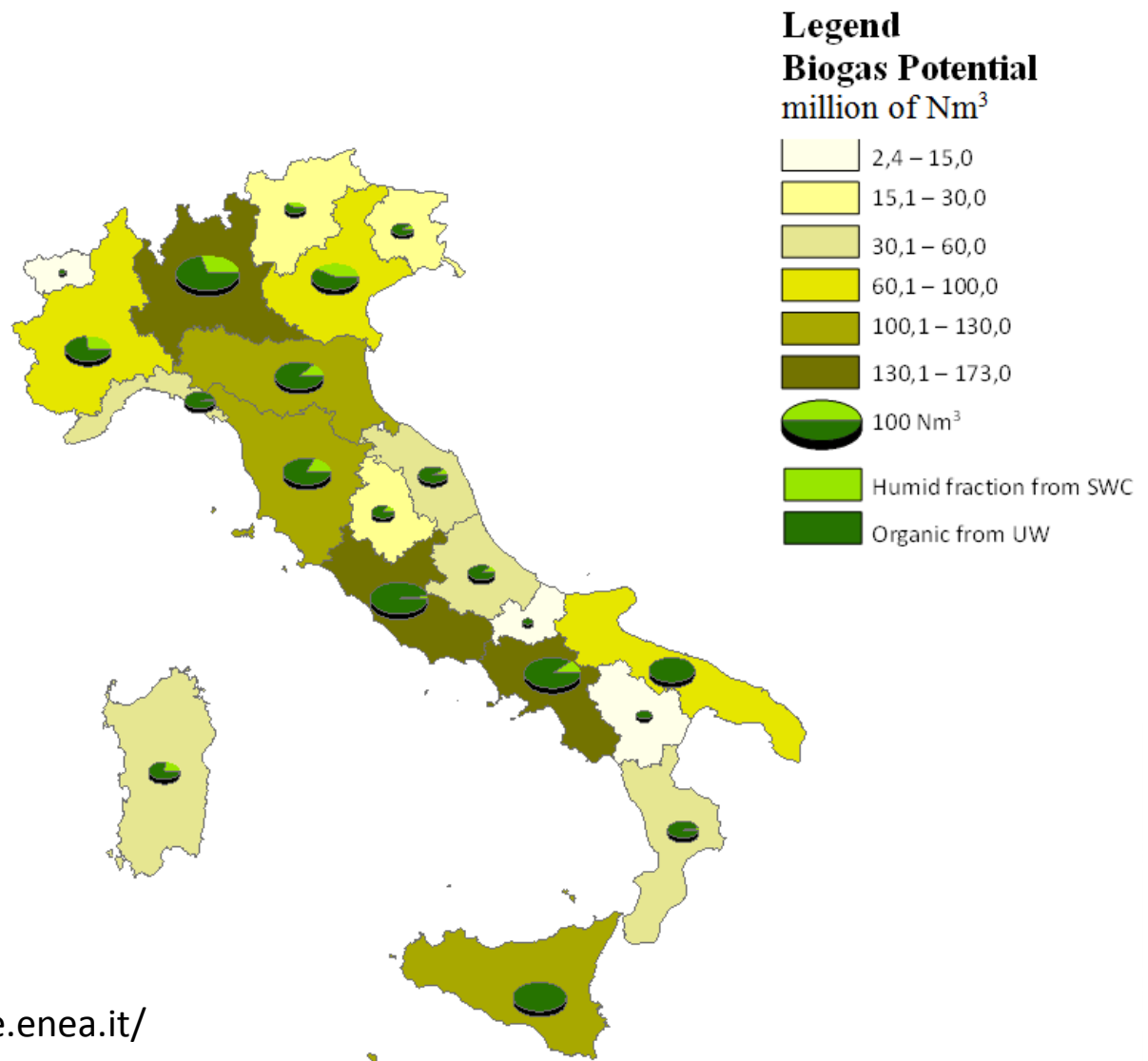
$1.9 \times 10^9 \text{ m}^3$

= 905 ktep potere calorifico

Potenziale totale

Residui vegetali e animali

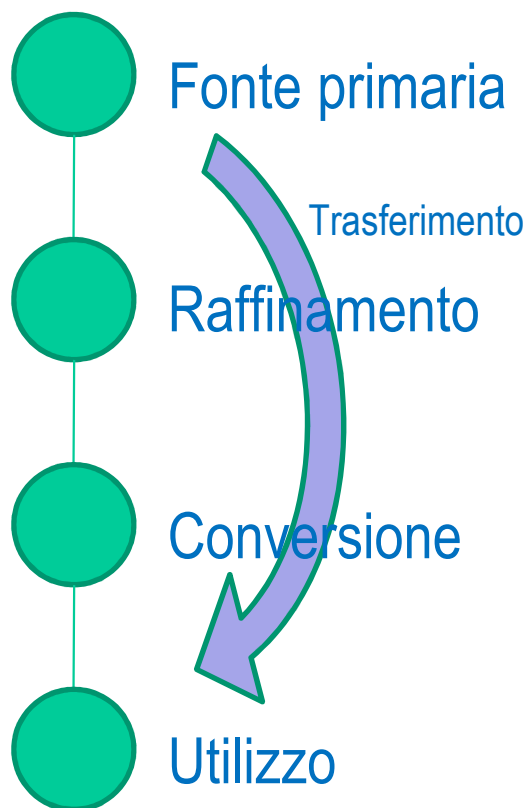
(ITABIA, 2007): 22 Mtep



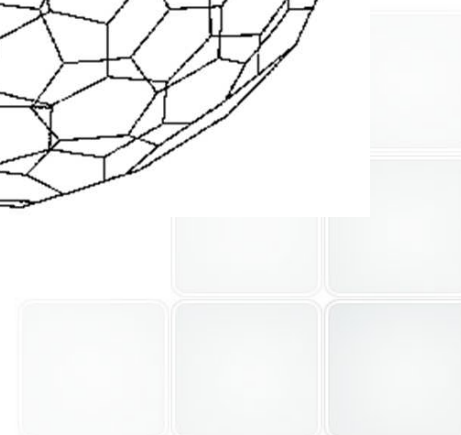
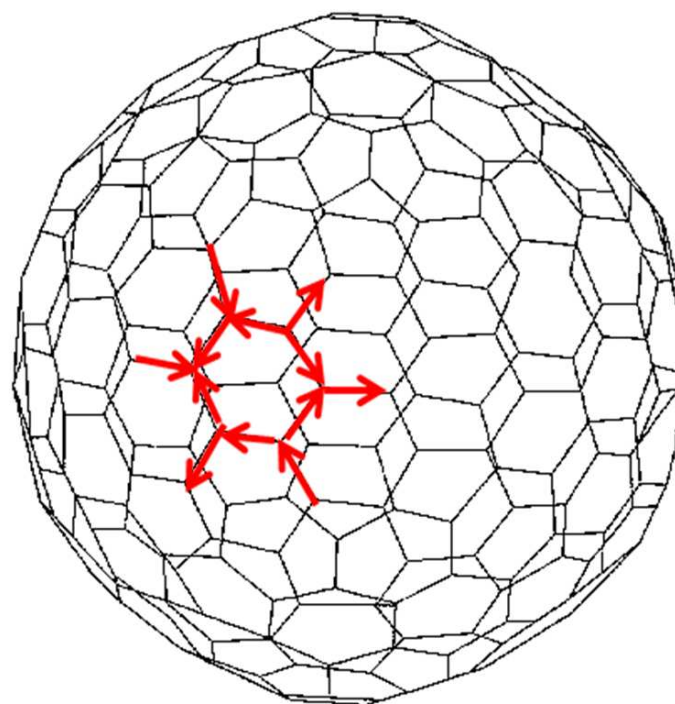
<http://www.atlantebiomasse.enea.it/>

Generazione distribuita

Sistema centralizzato

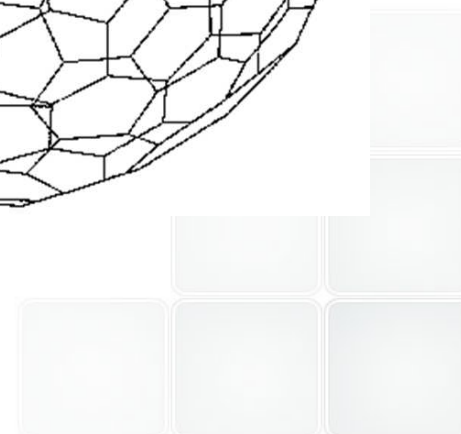
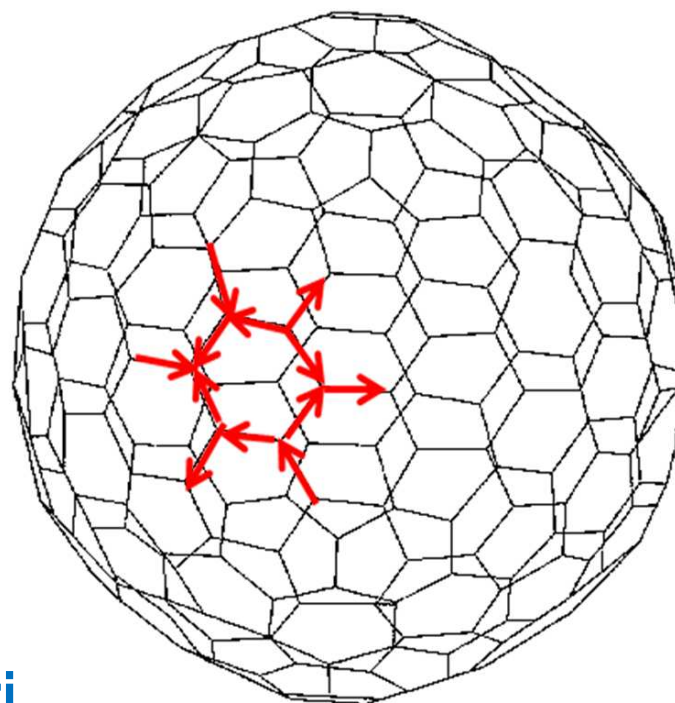


Sistema distribuito

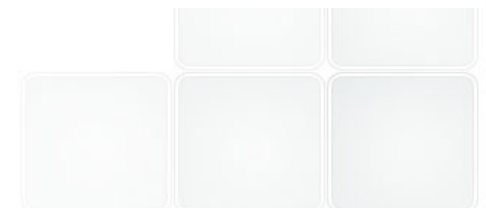
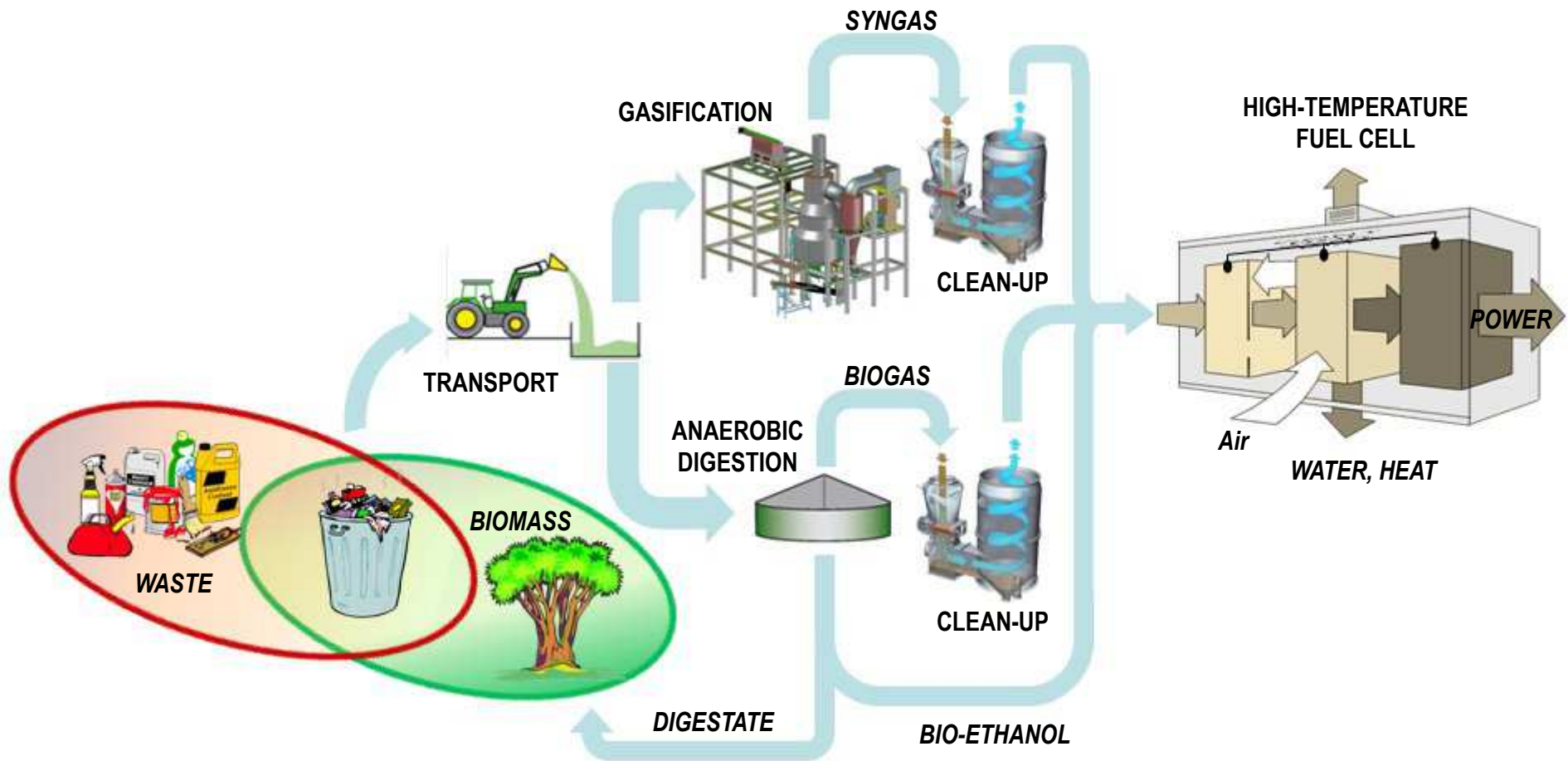


Sistema distribuito

- Fonti e produttività locali
 - Piccole quantità, maggiore efficienza
 - Flusso reticolato
 - Equilibrio diffuso
- essenziale per valorizzazione di rifiuti



Sistema-tipo



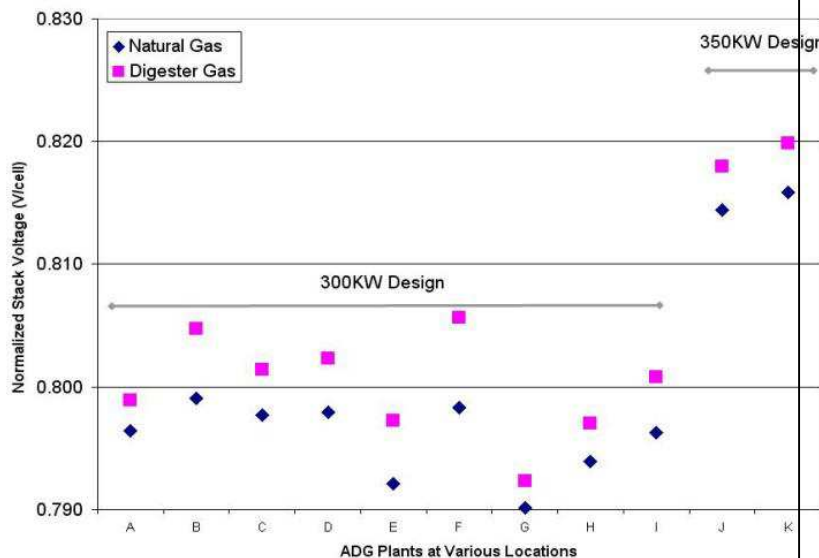
Biogas: Clean-up



Composizione:

- CH₄ 50-70%
- CO₂ 30-40%
- H₂ 0-1%
- N₂ 0-10%

Prestazioni biogas vs. gas naturale:
(FuelCell Energy, USA)
Contaminanti Most Wanted



H ₂ S	mg/m ³	0-5000 Ø 500	0-500 Ø 60	-
COS	mg/m ³	-	0,1-10	-
Merkaptane		-	-	-
Thiophene	mg/m ³	-	-	-
Sulfur compounds (Sulfide...)	mg/m ³	Ø 0,1	-	-
Σ Sulfur	mg/m³	0-5000	20 - 2500	0,1

cis-1,2-Dichlorethen / cis-1,2-dichloroethene	mg/m ³	0,03 - 0,13	0,3 - 0,7	
1,2-Dichlorethan / 1,2-dichloroethane	mg/m ³	0,007 - 0,13	0,1 - 0,4	
Vinylchlorid / Vinyl chloride	mg/m ³	0,002 - 0,59		
1,1,2-Trichlorethan / 1,1,2-trichloroethane	mg/m ³	< 0,005		
1,1,1,2-Tetrachlorethan / 1,1,1,2-tetrachloroethane	mg/m ³	< 0,01		
1,2-Dichloropropan / 1,2-dichloropropane	mg/m ³	0,005 - 0,01		
1,3-Dichloropropan / 1,3-dichloropropane	mg/m ³	0,005 - 0,007		
2,2-Dichloropropan / 2,2-dichloropropane	mg/m ³	0,005 - 0,007		
Chlorbenzol / chlorobenzene	mg/m ³	0,3 - 4,0	0,16 - 0,4	
Dichlorbenzol / Dichlorobenzene	mg/m ³	0,8 - 1,7	0,05 - 0,2	
Σ Halides (Cl, F, I, Br)	mg/m³	2,0 / 1,5 / 2,0	-	0,2

MOH (Trimethylsilanol)	mg/m ³	2,2 - 3,4	0,03 - 0,15	-
L2 (Hexamethyldisiloxan)	mg/m ³	0,4 - 0,8	0,01 - 0,08	-
L3 (Octamethyltrisiloxane)	mg/m ³	0,04 - 0,3	0,08 - 0,2	-
L4 (Decamethyltetrasiloxane)	mg/m ³	0,1 - 0,1	-	-
D3 (Hexamethylcyclotrisiloxan)	mg/m ³	0,3 - 0,5	0,3 - 0,4	-
D4 (Octamethylcyclotetrasiloxan)	mg/m ³	4,0 - 5,3	6,6 - 8,7	-
D5 (Decacylcyclopentasiloxan)	mg/m ³	0,1 - 0,6	9,1 - 17,5	-
Σ Siloxanes	mg/m³	7,1 - 10,6	16,1 - 27,0	0,2

Biogas: Clean-up

Rispetto ad applicazioni convenzionali:
altissima purità richiesta...

→ Abbattimento emissioni si sposta
a monte del generatore



MCFC stack corrosion by halogenated HCs

H ₂ S	mg/m ³	0-5000 Ø 500	0-500 Ø 60	-
COS	mg/m ³	-	0,1-10	-
Merkaptane		-	-	-
Thiophene	mg/m ³	-	-	-
Sulfur compounds (Sulfide...)	mg/m ³	Ø 0,1	-	-
Σ Sulfur	mg/m³	0-5000	20 - 2500	0,1

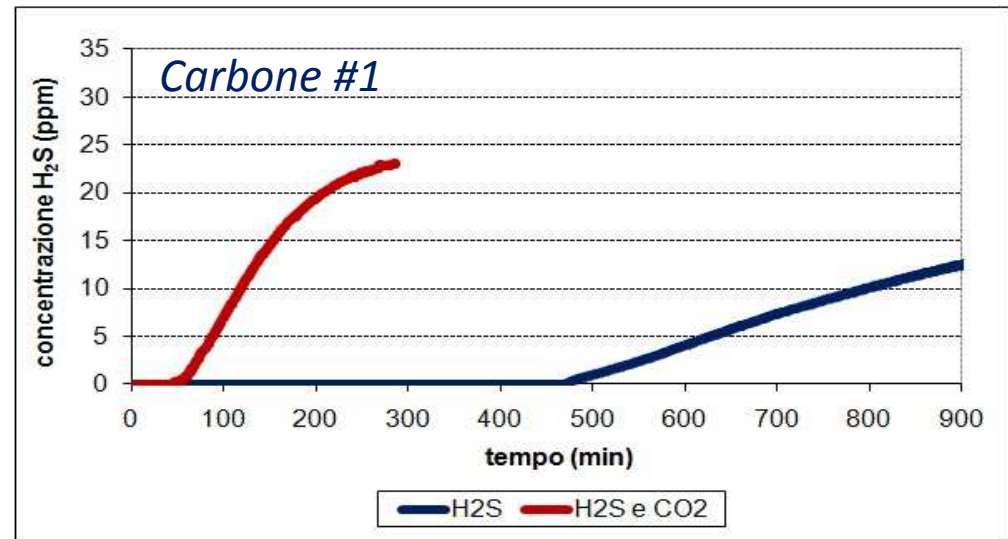
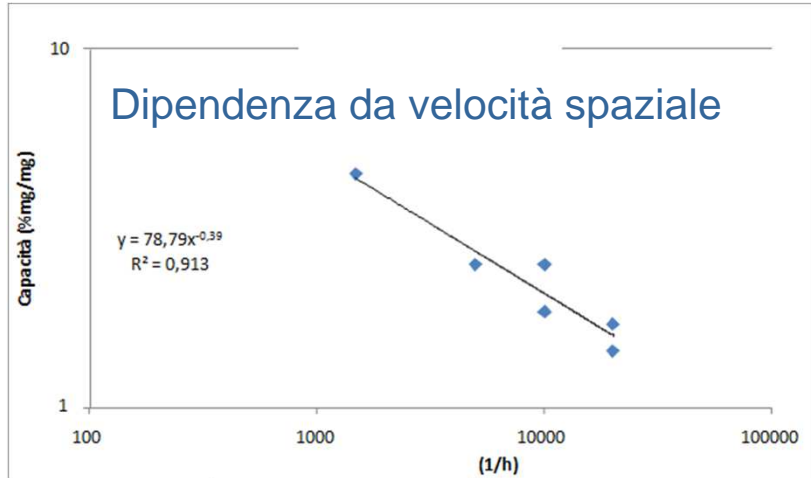
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Vinylchlorid / Vinyl chloride	mg/m ³	0,002 - 0,59		
1,1,2-Trichlorethan / 1,1,2-trichloroethane	mg/m ³	< 0,005		
1,1,1,2-Tetrachlorethan / 1,1,1,2-tetrachloroethane	mg/m ³	< 0,01		
1,2-Dichloropropan / 1,2-dichloropropane	mg/m ³	0,005 - 0,01		
1,3-Dichloropropan / 1,3-dichloropropane	mg/m ³	0,005 - 0,007		
2,2-Dichloropropan / 2,2-dichloropropane	mg/m ³	0,005 - 0,007		
Chlorbenzol / chlorobenzene	mg/m ³	0,3 - 4,0	0,16 - 0,4	
Dichlorbenzol / Dichlorobenzene	mg/m ³	0,8 - 1,7	0,05 - 0,2	
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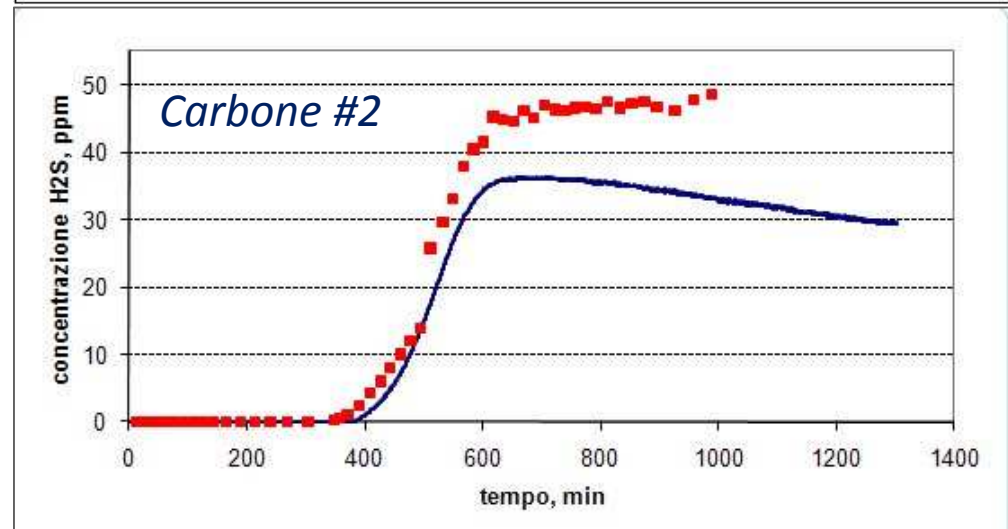
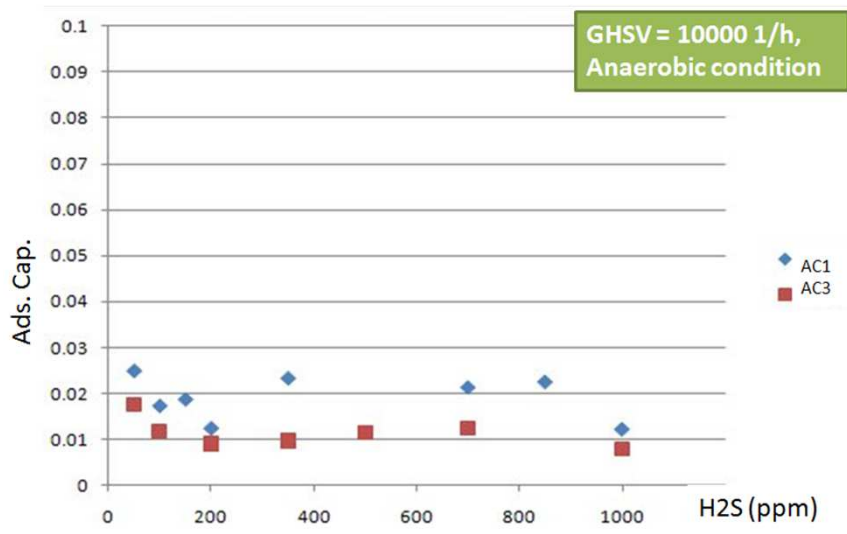
Biogas: Clean-up



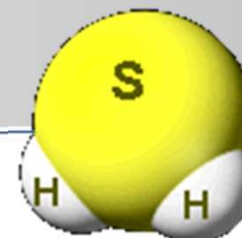
Prestazioni carboni impregnati – abbattimento H₂S in presenza di CO₂



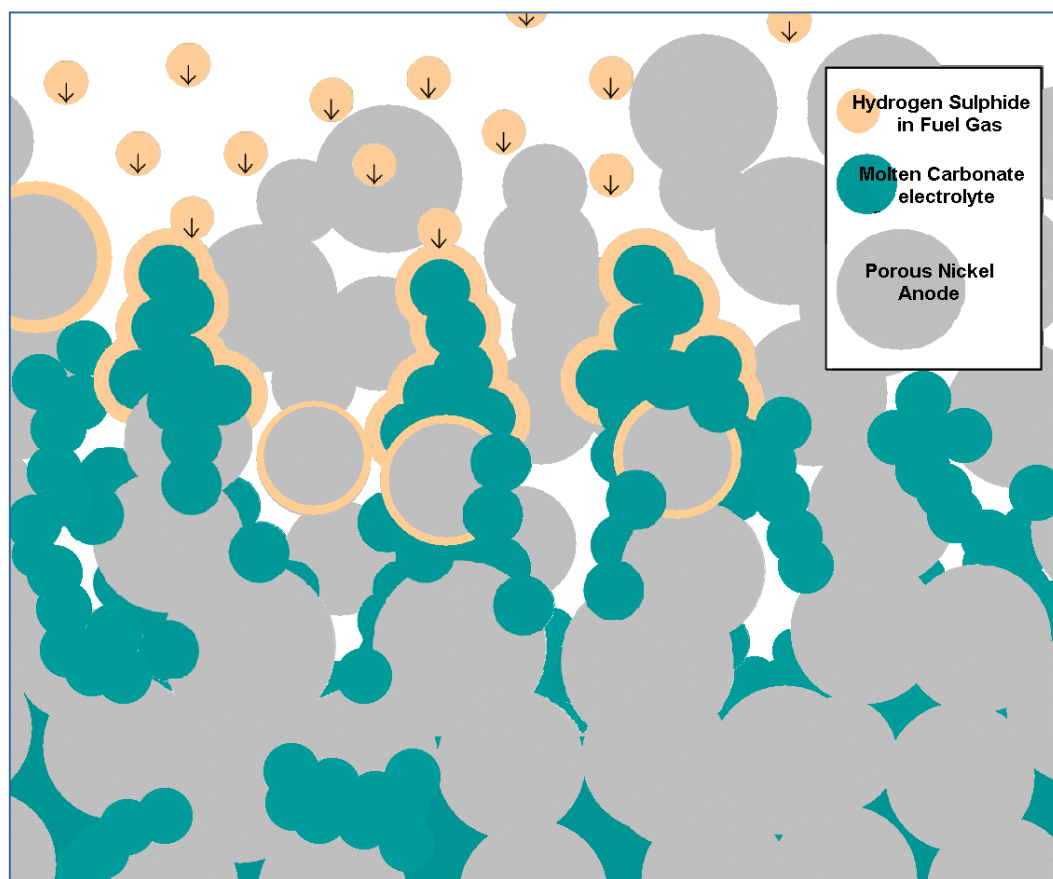
Dipendenza da concentrazione in ingresso



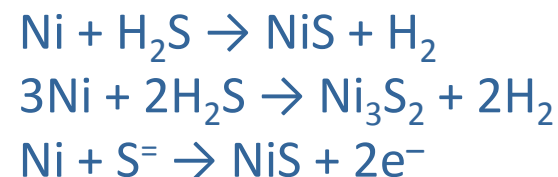
Biogas: uso in celle a carbonati fusi



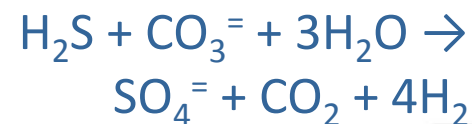
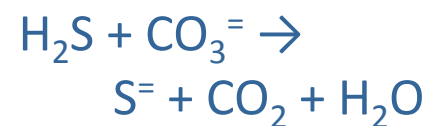
Avvelenamento: disattivazione *anodo* ed *elettrolita*



Anodo

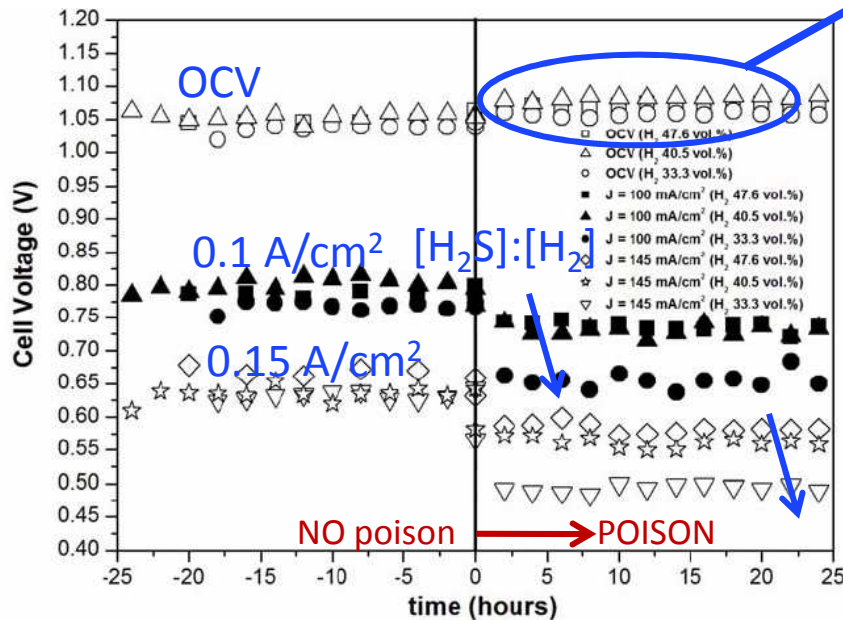
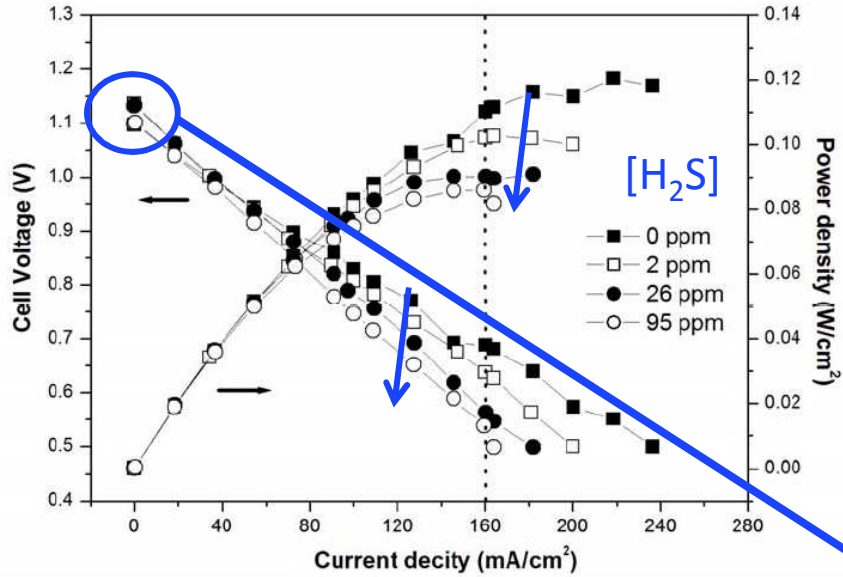
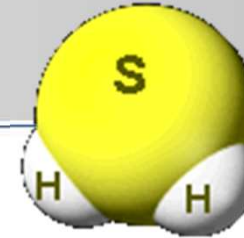


Elettrolita



Dipendenze: *Temperatura, concentrazione H₂S, tempo d'esposizione, proporzione H₂S:H₂:O₂, densità corrente, fuel utilization, materiale, copertura zolfo*

Biogas: use in celle a carbonati fusi



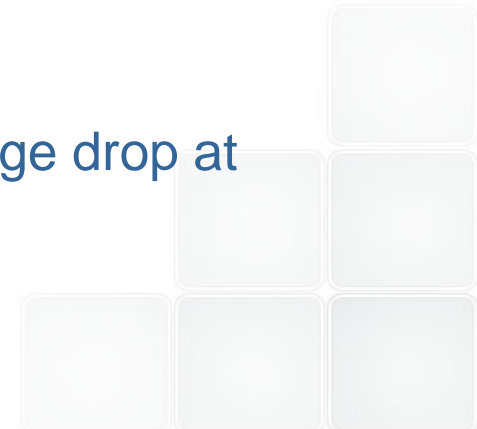
Polarization curves:

- Increased cell voltage drop at higher bulk H₂S
- Especially at high current densities (>50mA/cm²)

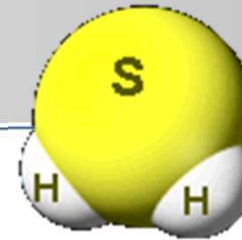
Slight change in OCV might indicate competition between H and S to react with Ni

H₂S:H₂ proportion:

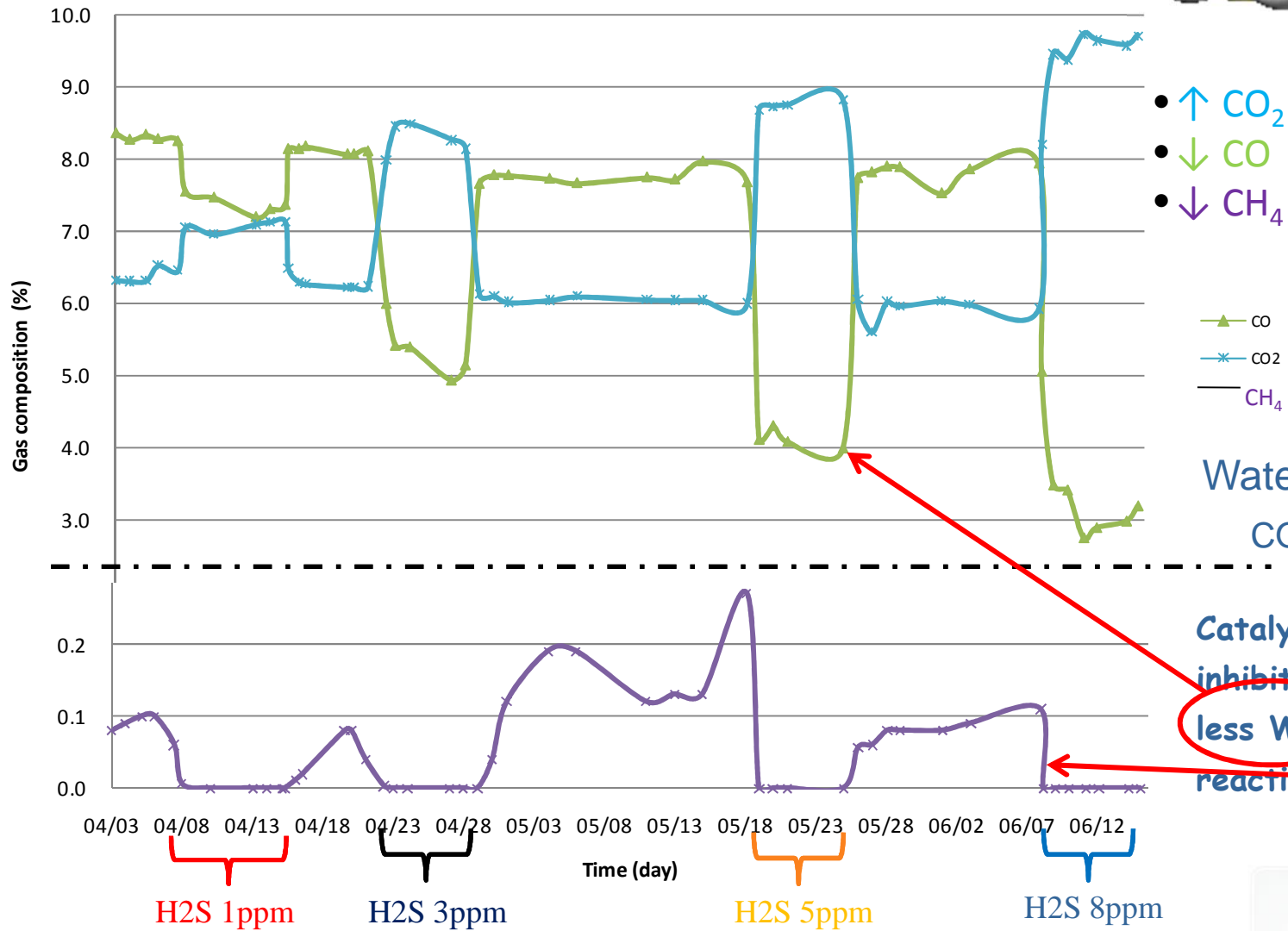
- Increased cell voltage drop at higher proportions



Biogas: uso in celle a carbonati fusi



Gas composition



Water-Gas Shift Reaction

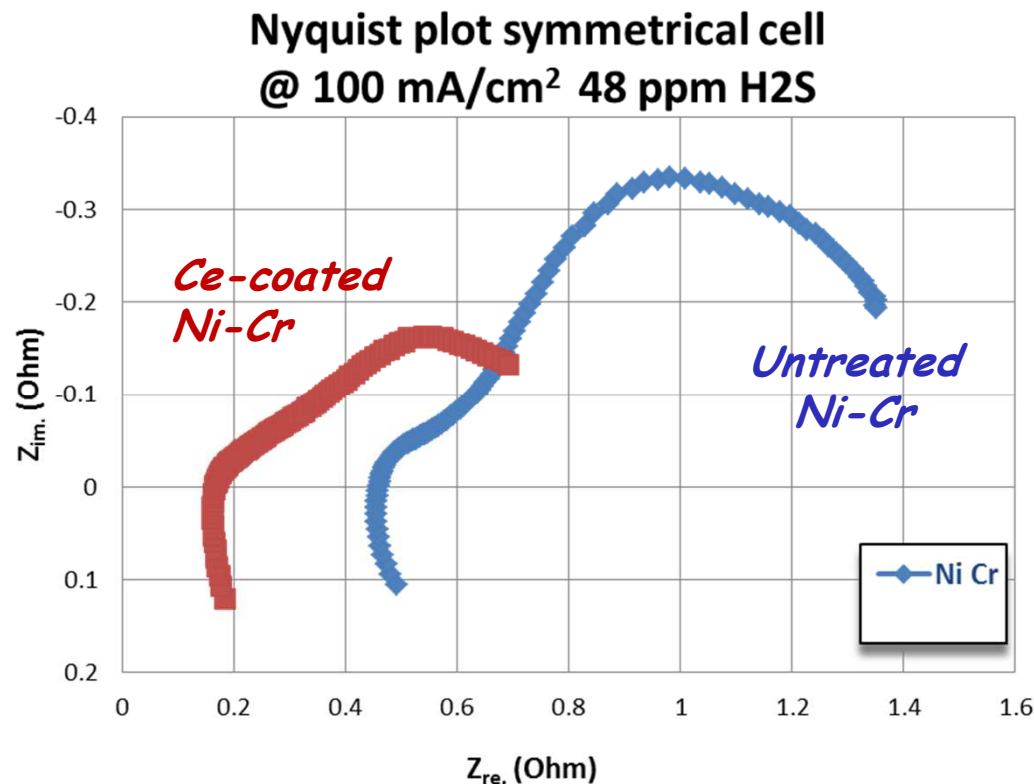


Catalytic activity of Ni inhibited by H₂S (barrier?):
 less WGS no secondary reactions (methanation...?)

MCFC: anodi alternativi



Industrial Ni-Cr anodes were dipcoated with Ceria to create sacrificial layer



Anode

H₂ = 3.5 NI/h (26%)

N₂ = 8.6 NI/h (64%)

CO₂ = 0.6 NI/h (4%)

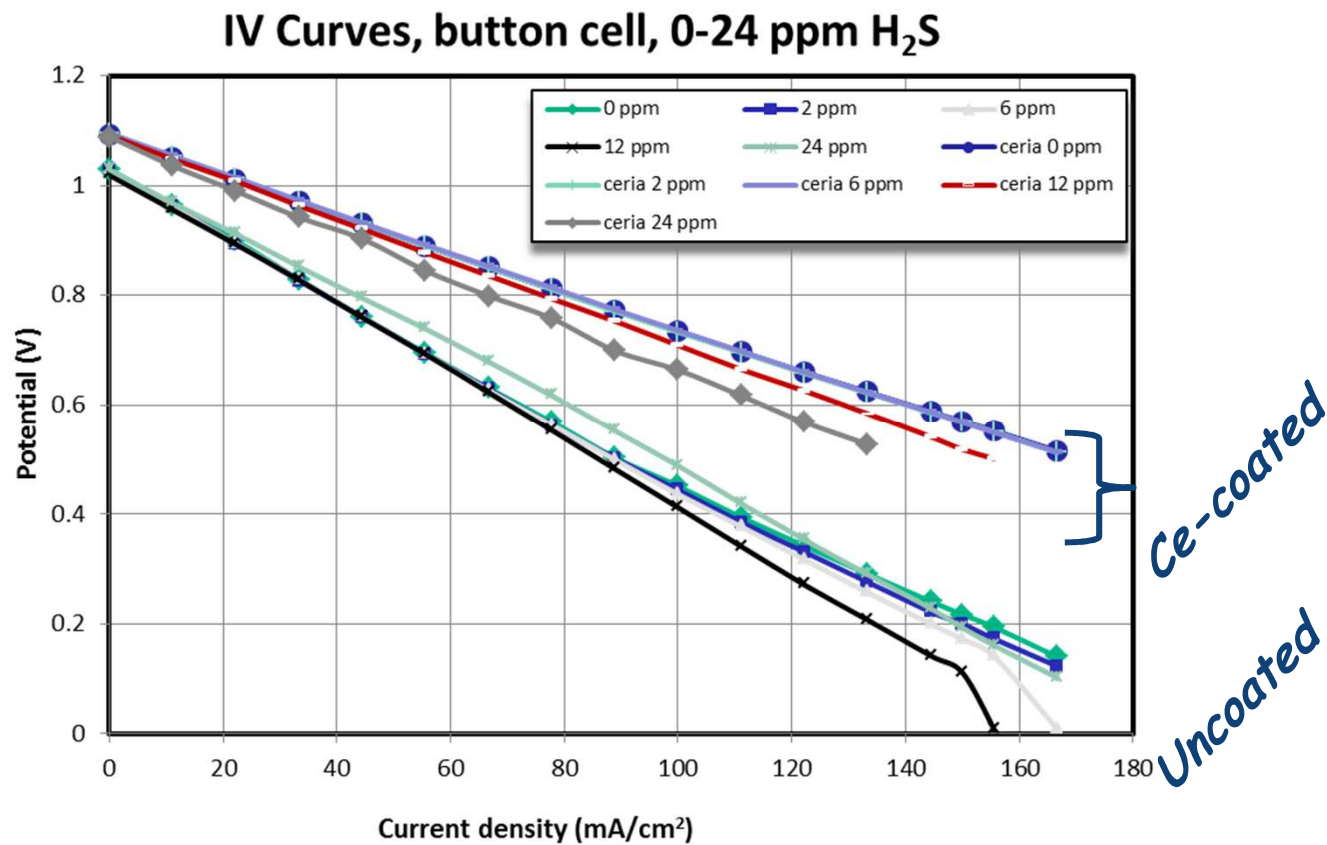
H₂O = 0.6 g/h = c.a. 0.7
NI/h @STP (5%)

→ Significant increase in H₂S tolerance!

MCFC: anodi alternativi



Industrial Ni-Cr anodes were dipcoated with Ceria to create sacrificial layer

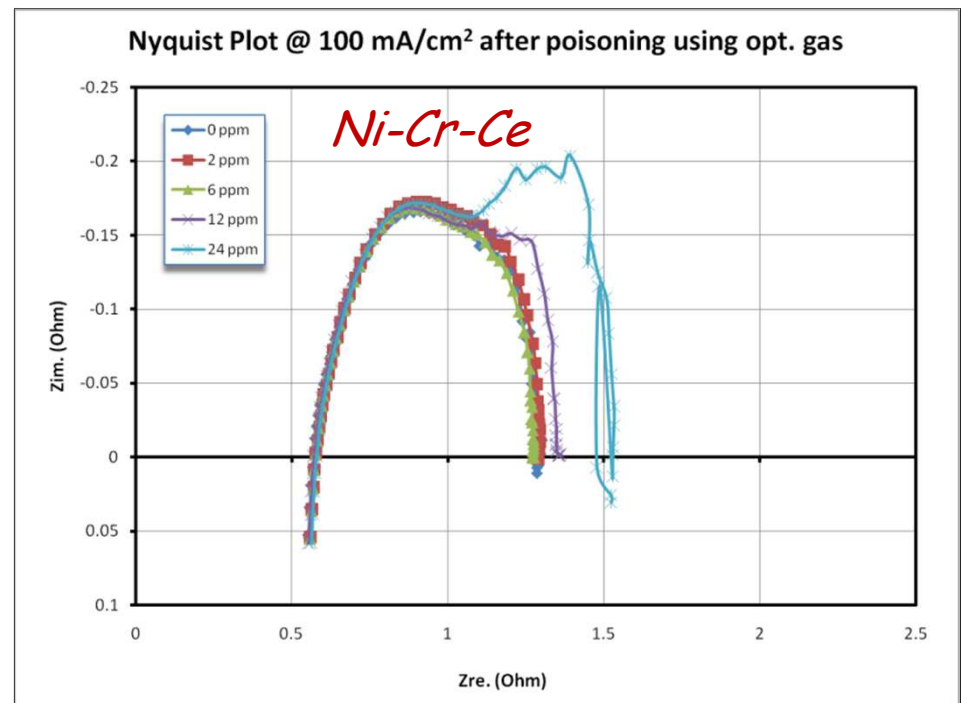
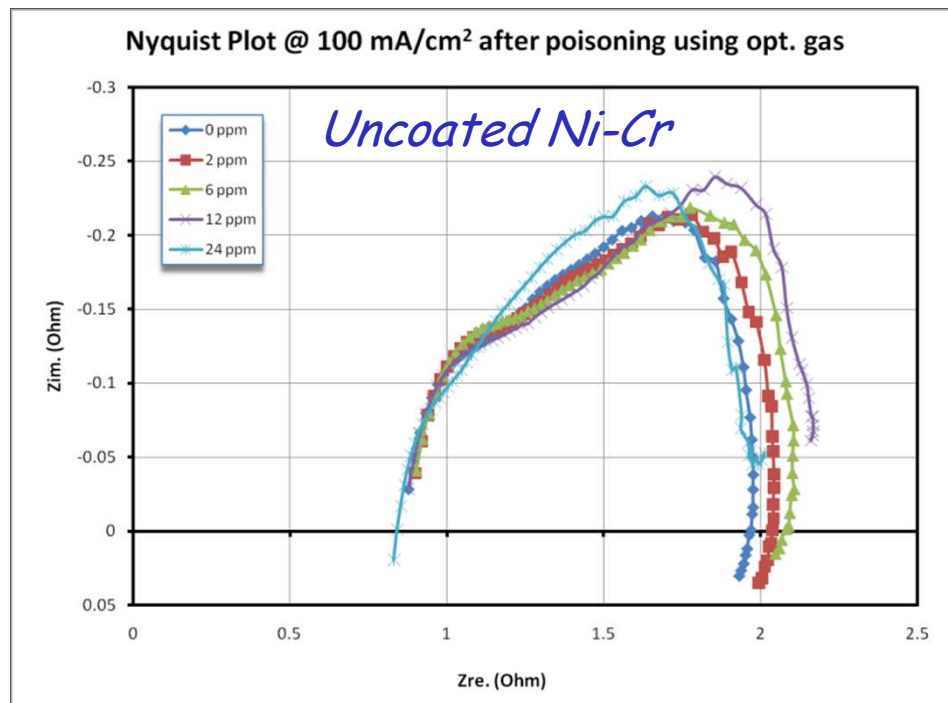


→ Significant increase in H₂S tolerance!

MCFC: anodi alternativi

Industrial Ni-Cr anodes were dipcoated with Ceria to create sacrificial layer

Button cell



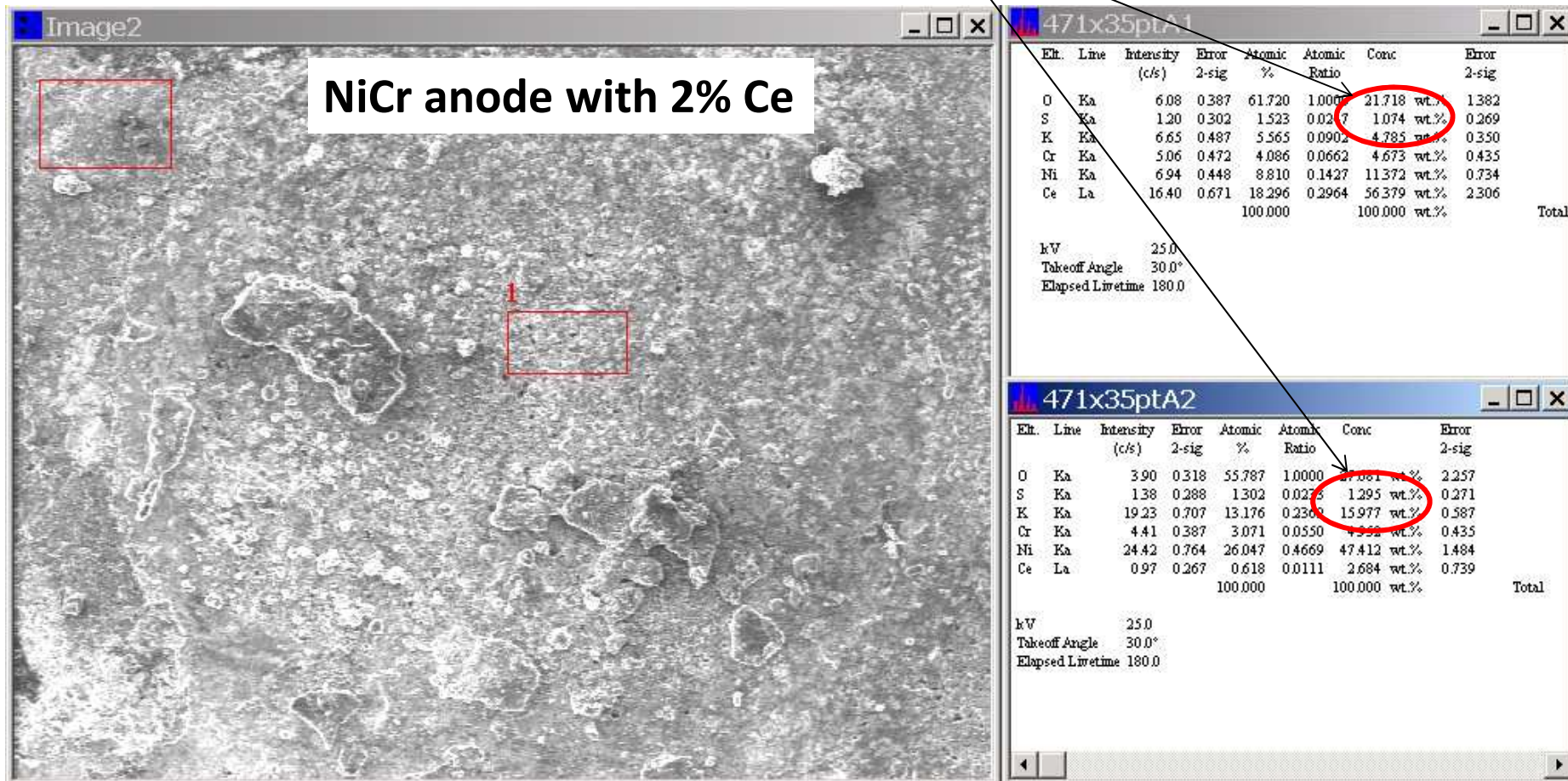
→ Significant increase in H₂S tolerance!

MCFC: anodi alternativi

Post-test analysis: XRD

Button cell

Significant amount of S trapped on Ce-coated anode

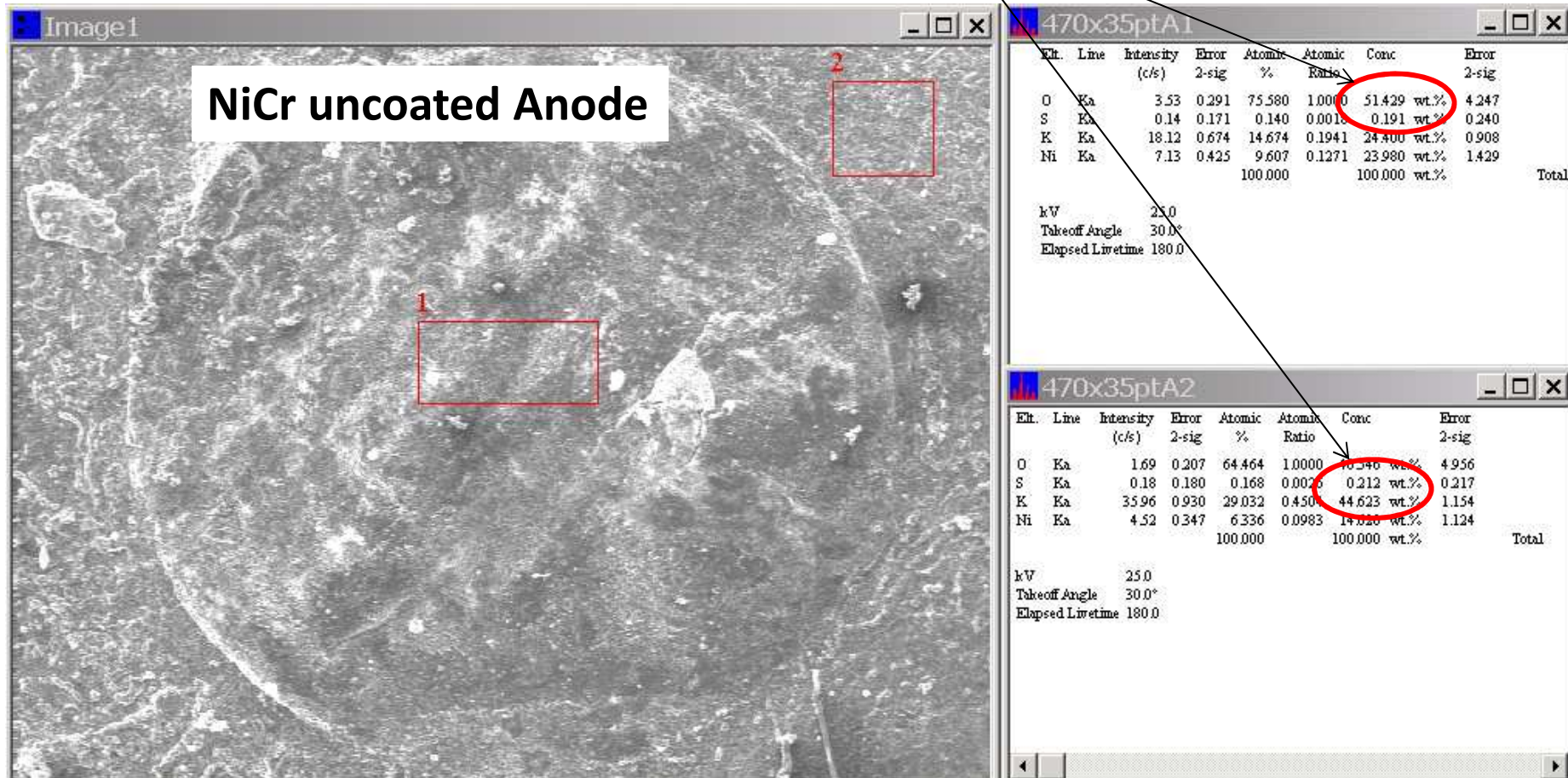


MCFC: anodi alternativi

Post-test analysis: XRD

Button cell

5 times less S compared to Ce-coated anode!



- **Potenziale energetico dei rifiuti è significativo: ma richiede alta efficienza!**
- **Valorizzazione rifiuti/biomasse stimola l'instaurarsi della generazione distribuita**
- **Uso di biogas in celle sposta il controllo delle emissioni a monte del generatore elettrico**
- **Clean-up possibile con metodi convenzionali... ma occhio alle condizioni!**
- **Venirsi incontro: MCFC con anodi più resistenti allo zolfo – primi risultati promettenti**
- **Rimane da investigare il meccanismo – complesso! – di avvelenamento**

Grazie...

Acknowledgements: G. Monteleone, V. Naticchioni, E. Simonetti, H. Devianto, V. Cigolotti, F. Zaza