


INSTYTUT NAFTY I GAZU
Państwowy Instytut Badawczy

„A környezetbiztonság szerepe és lehetőségei az EU pályázati rendszer tükrében"
19-21 October, 2015 Lillafüred, Palotaszálló , Hungary

Biocatalyzed silicate gel intended for use in geothermal industry – Experimental experiance and challanges

S. Falkowicz, R. Cicha-Szot — Polish Oil & Gas Institute National Research Institute

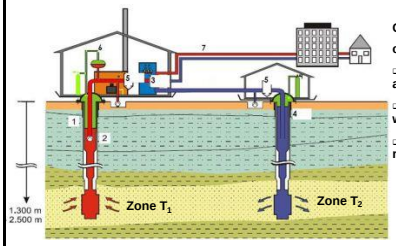
S.A. Bailey — Flex-Chem Corporation Weatherford, OK USA

Questions

- Why do we need to use conformance technology in low temperature thermal water reservoirs?
- Why should microbes be used in geothermal wells?
- What are the limitations of silicate system? How can they be eliminated?
- What are the strength and durability of the gel system?
- What are the challenges?

Idea of thermal water exploitation

Poland has natural sedimentary structural basins filled with geothermal waters of diversified reservoir temperatures, from 20 to 80–90°C, in some cases even over 100°C.



Geothermal waters in Poland can be used for:

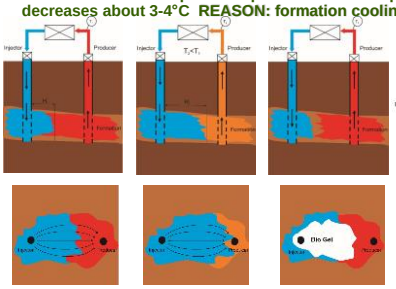
- **heating of private houses and industrial buildings,**
- **for preparation of warm water,**
- **and for therapeutic and recreational purposes.**

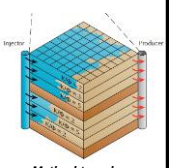
Kępińska, 2015
Górecki et al., 2014
Gringarten, 1978

Dublet type development scheme – maintain the reservoir pressure and insure an indefinite supply of water, permits the recovery of heat contained in the rock.

The influence of reservoir anisotropy on thermal water exploatation efficiency

In some cases after specific exploitation time temperature of water decreases about 3-4°C REASON: formation cooling phenomena



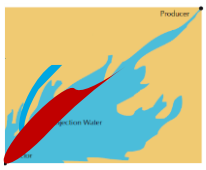


Method to enhance recovery from geothermal field
Patent Nº 386273

When temperature of water decreases the flow path can be changed to increase access to additional zones using permeability modification

Idea of biocatalyst triggered silicate system

- Enhancing recovery from geothermal fields is based on changing preferential pathways of the geothermal water in the exploited field through introduction of colloidal silicate solution by injection well
- Modification of formation permeability is in strictly defined high permeability channels between injector and producer
- Plugging the high permeability channel diverts flow into other zones and as a result increases communication time and heat recovery between injection and exploitation well.



Source:https://en.wikipedia.org/wiki/Mono_Lake

Do you know what is the number of microbes on the Earth ?

5 Nonillions
5*10^{30}

SL-1A

SL-2A

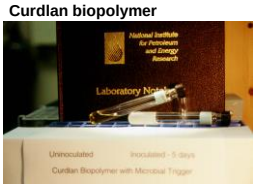
Alkaliphilic, metabolically active at pH 11 and become metabolically inactive at pH <7

20 – 40 ºC

Hypersalinity and high alkalinity pH10

Alkaliphilic microbial gel system

Curdlan biopolymer



Sol ↔ Gel

pH 10.0 ↔ 9.5

Permeability modification with gel systems

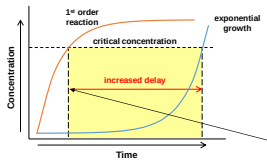
- Interconvertible between soluble form and gel form through delayed triggering mechanism
  - Injectable into formation as low-viscosity gelant (Sol)
  - Triggered in situ to form barrier (Gel)
- pH sensitive gel systems require acid production in situ

Alkaliphilic microbial gel system

Biocatalyst trigger

Urea,esters, crosslinkers -

- The rate of product formation is fastest initially when the reactants are at high concentration



Acid production from exponentially growing biocatalyst delays start of gelation

Permeability modification with gels

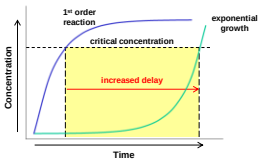
- Injectable into formation as low-viscosity gelant (Sol)
- Triggered in situ to form barrier (Gel)
- Delayed gelation requires acid production in situ

Limit of gel placement, and gel strength

Bailey et al., 2000

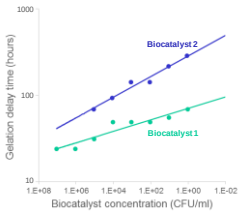
Alkaliphilic microbial gel system

Biocatalyst trigger



Acid production from exponentially growing biocatalyst delays start of gelation

Gelation delay with biocatalyst

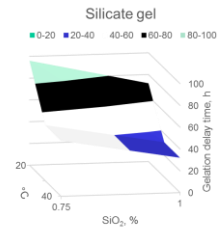


Alkaliphilic microbial gel system

Silica based gelants

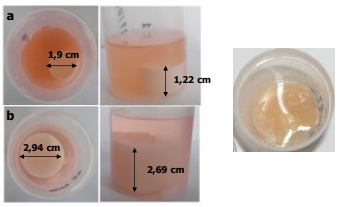
- Silicate gelants
  - Economical
  - Stable for deep injection
- Gelable by delayed triggers
  - External (electrolyte, heat)
  - Internal (pH)
- Biocatalyzed gelation
  - Internal
  - Delay 2-12 days

Gelation delay with biocatalyst



Disadvantages of Biocatalyzed Silicate Gel (BSG)

- **Obtained samples of BSG were rigid but brittle and shrank substantially**



- **To overcome the disadvantages specially selected improvements/ additives of silicate gel properties were developed**

Lakatos et al., 1999
SPE 56739

Gelant formulation

TARGET: Preparing stable silicate solution based on commercially available technical grade chemicals

Sodium silicate solutions screened

Trade name	assay mark	Na_2O/SiO_2	Silica modulus	Na_2O %	SiO_2 %	density g/cm³	pH
R-145	A	2.42	2.50	11.8	28.60	1.46	11.9
R-149	B	2.71	2.80	11.9	32.30	1.50	11.6
R-140	C	2.91	3.00	9.93	28.87	1.42	11.3
R-137	D	3.10	3.20	8.83	27.37	1.37	11.1
R-132	E	3.26	3.37	7.61	24.79	1.33	11.1

Gelant formulation

Stability of product C and D at pH 11 with different concentrations of silica and salt

	SiO_2, %	NaCl, % 3
C	5	L_3
	6	L_3
	7	L_3
	8	L_3
D	5	L_3
	6	L_3
	7	L_{16}
	8	L_{16}

	SiO_2, %	NaCl, % 4
C	3	32h
	4	L_3
	5	L_3
	6	L_3
D	3	32h
	4	L_3
	5	L_3
	6	L_3

Stability of product D at different pH and silica content

SiO_2, %	pH 10	9	8	7
1	1h	1h	45 min	30min
2	6h	5h	3h	2h
3	6h	6h	4h	2h
4	19h	17h	15h	12h
5	31h	22h	19h	NS
6	67h	43h	37h	NS

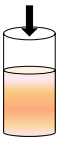
L_3 – liquid stable for x days duration of screening experiment
NS – Not stable, sedimentation immediately upon mixing

Defining gelling parameters

TARGET: elimination of critical disadvantages – shirkage and brittlness

Sodium silicate 3% NaCl

Sodium silicate 3% NaCl + modifier



Modifiers:

- **Polymers**
- **Biopolymers**
- **Amphoteric metals Fe, Al**

No toxic or regulated chemicals

Sol-gel transition may be triggered by

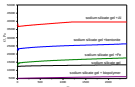
- **External catalysis CO_2**
- **Internal catalysis (for example urea)**
- **Biocatalysis**

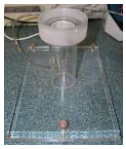
Cicha-Szot et al., 2010

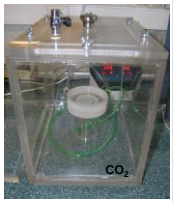
Bulk tests

"Everything that can be invented has been invented."

Charles H. Duell, Commissioner of the United States Patent and Trademark Office, 1899



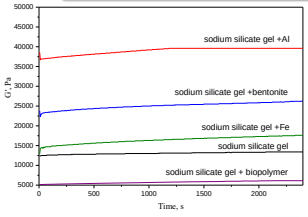




Modification of Biocatalyzed Silicate Gel (BSG)

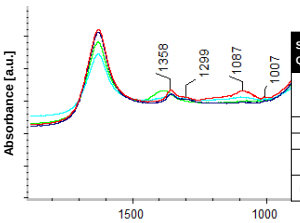
Additieves to improve mechanical properties of the gel

- **A Curdlan → Modification with protein**
- **B Fe**
- **C Al → G' ↑ 23kPa; shrinkage 1,1%**
- **D Bentonite**



Dynamic Mechanical analysis

Modification of Biocatalyzed Silicate Gel (BSG)



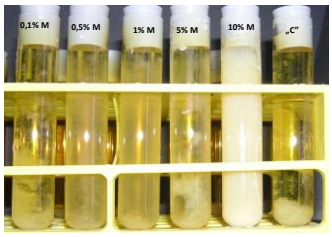
Shift in band position that represent Si-O-Si Q^2

Designation	Solution	pH	Wave number [cm⁻¹]
A red	D3.3	8	1007
B blue	D3.3 + Al	7	1018
C green	D3.3 + curdlan	10	1001
D light blue	D3.3 + NanoSil	9	1004

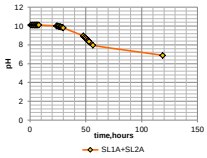
FTIR-ATR results of modified silicate systems

Cicha-Szot et al., 2014

Gelling



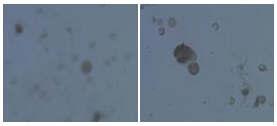
decrease caused by co-inoculated strains SL1A and SL2A



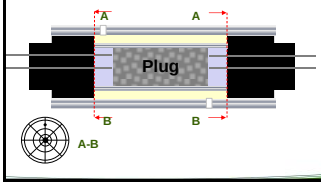
Solution of water glass containing strains SL1A and SL2A (pH 10,97) after 24h (magnitude 60x0,85)

Bulk/Coreflooding tests

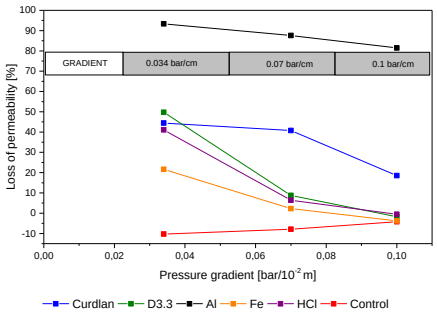
Solution of water glass containing strain SL2A (pH 11,09) after 24h (magnitude 20x0,5)



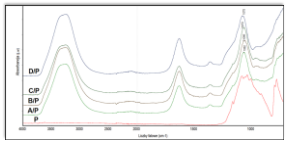
Solution of water glass containing strain SL2A (after 48 hours) pH 10,93 - precipitation of SiO_2xNa_2O



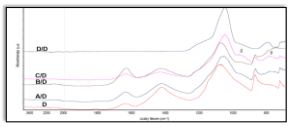
Results of permeability modification tests

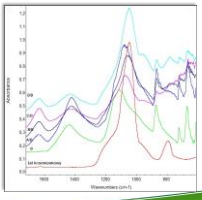


Results of permeability modification tests



Designation	Solution
A	D3.3
B	D3.3 + Al
C	D3.3 + curdlan
D	D3.3 + NanoSil



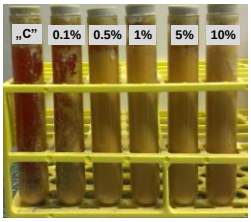


FTIR-ATR results of modified silicate systems – interaction with rocks (sandstone, dolomite)

Results of permeability modification tests

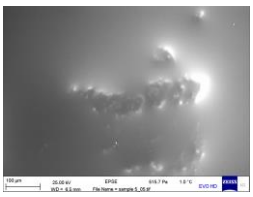
2012

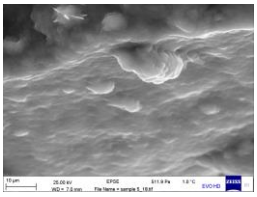
2015



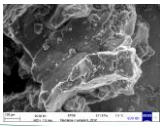
After over two years of storing tests confirmed expected durability of biocatalyzed silicate gel

Results of permeability modification tests





Hydrogel, free water removed structure of gel visible, sample still fully hydrated.



Hydrogel, free water removed structure of gel visible, sample still fully hydrated.

CONCLUDING REMARKS

- One of the most promising agents to shutting off reservoir zones with high permeability rocks are silicate gels with addition of biocatalyst used for pH control of treatment fluid
- That kind of systems permit significant extension of the injection time of low viscosity alkaline silicate solutions – **from a few to a few hundred hours**
- Coreflooding experiments proved required strenght and durability of BSG system
- Properly applied BGS can extended economic life of geothermal reservoirs
- Environmentally friendly
- Based modified sodium silicate solution may be trigger by CO_2 – preventing leakeges in CCS projects

CHALLANGES

- Higher temperatures
- Upscalling
- Project development and implementation

Thank you for your attention!

INSTYTUT NAFTY I GAZU
Państwowy Instytut Badawczy
ul. Lubicz 25 A, 31-503 Kraków

www.inig.pl
office@inig.pl