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Accelerating DeepTech Innovation

Factors impacting cement integrity

Introduction

1

Hydrocarbon wells are often drilled in a CO_2 , H_2S and/or a high temperature environment. These gases and/or high temperature can degrade set cement, negatively impacting cement integrity.

2

Workover, stimulation, EOR and similar interventions in a well may also impact cement sheaths inside a well.

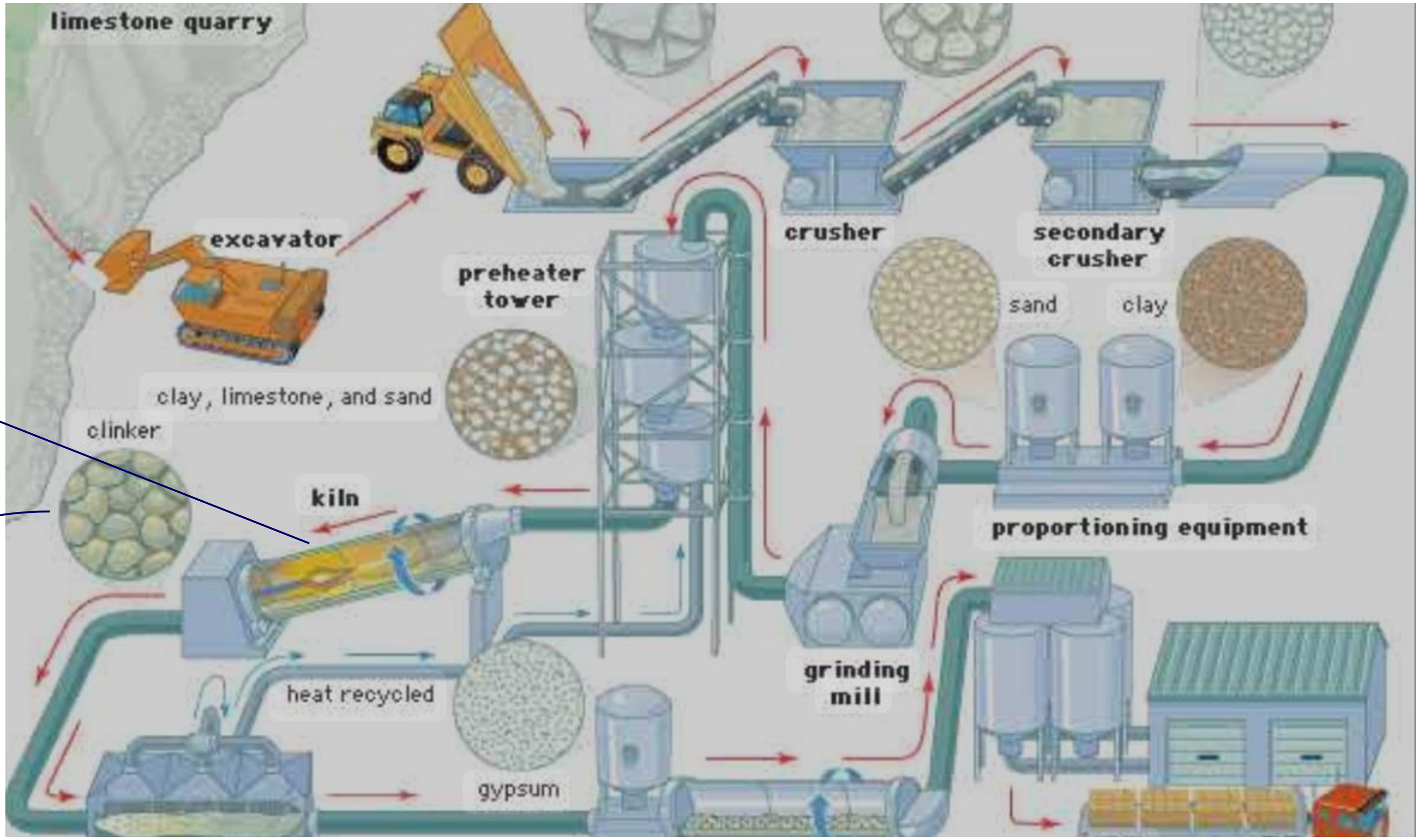
3

It is important to understand how these factors may lead to structural failures of set cement, so a mitigation strategy can be put in place and extend the life of the well.

Cement manufacturing

Forno rotativo de clinquerização em Cantagalo
(Lafarge, 2011)

Clinker



Joseph Aspdin, 1824

Clinker Composition

Compound	Abbreviation	Chemical Formula	%	Contribution on performance
Tricalcium Silicate (Alite)	C_3S	$3\ CaO.\ SiO_2$	45 - 60%	Durability and total resistance
Dicalcium Silicate (Belite)	C_2S	$2\ CaO.\ SiO_2$	15 - 30%	Long term durability
Tricalcium aluminate	C_3A	$3\ CaO.\ Al_2O_3$	5 - 12%	Durability and early setting
Tetracalcium aluminoferrite	C_4AF	$4\ CaO.\ Al_2O_3\ Fe_2O_3$	6 - 12%	No effect on durability
Gypsum (added during grinding)	CSH_2	$CaSO_4\ 2H_2O$	2 - 10%	Prevents early setting

Types of Cement

API Class	Depth		Temperature		Composition
	ft	m	°F	°C	
A-C	60000	1830	80 - 170	27 - 77	Low C3A No retarder
F	10000 - 16000	3048 - 4877	230 - 320	110 - 160	Low C3A Retarder present
G, H	-	-	80 - 200	27 - 93	Coarse - grained Type II & Type V portland cement No retarder
J	> 20000	> 6100	> 350	> 177	Essentially beta dicalcium silicate & pulverized sand

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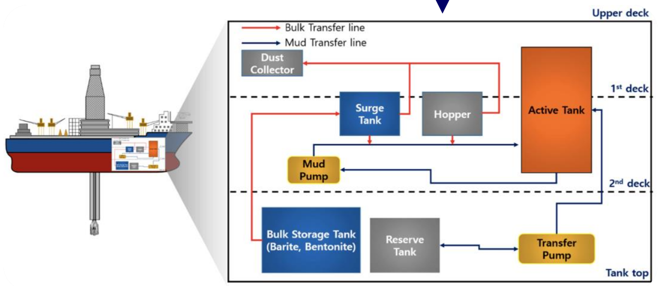
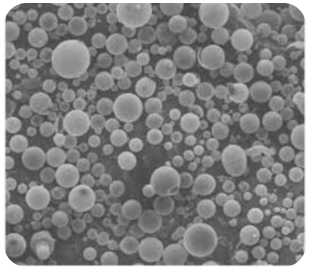
Cement Logistics (pathways)

Cement Logistics (pathways)



Slurry design / laboratory testing

+



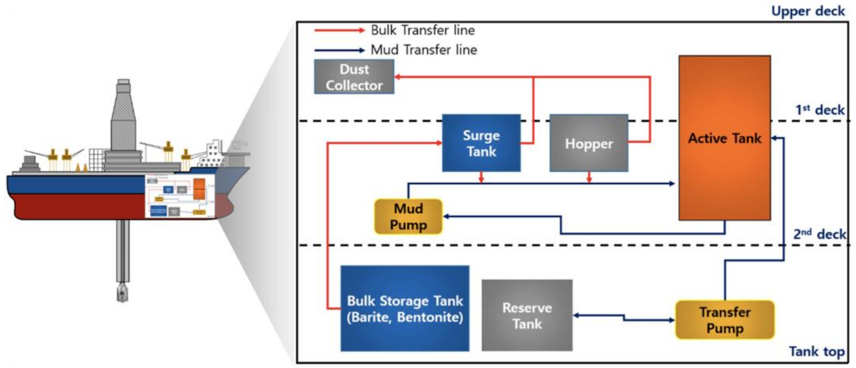
3M glass bubbles

...

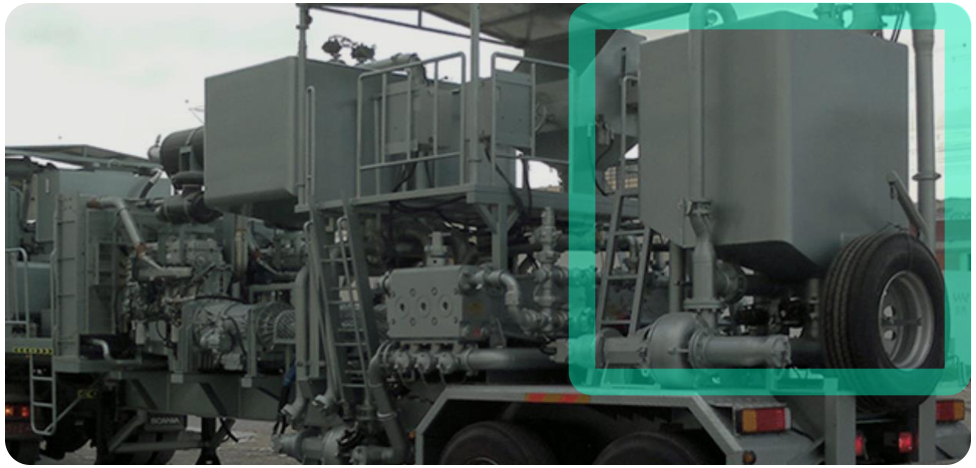
Micro Silica (Silica Fume)

Cement Logistics (pathways)

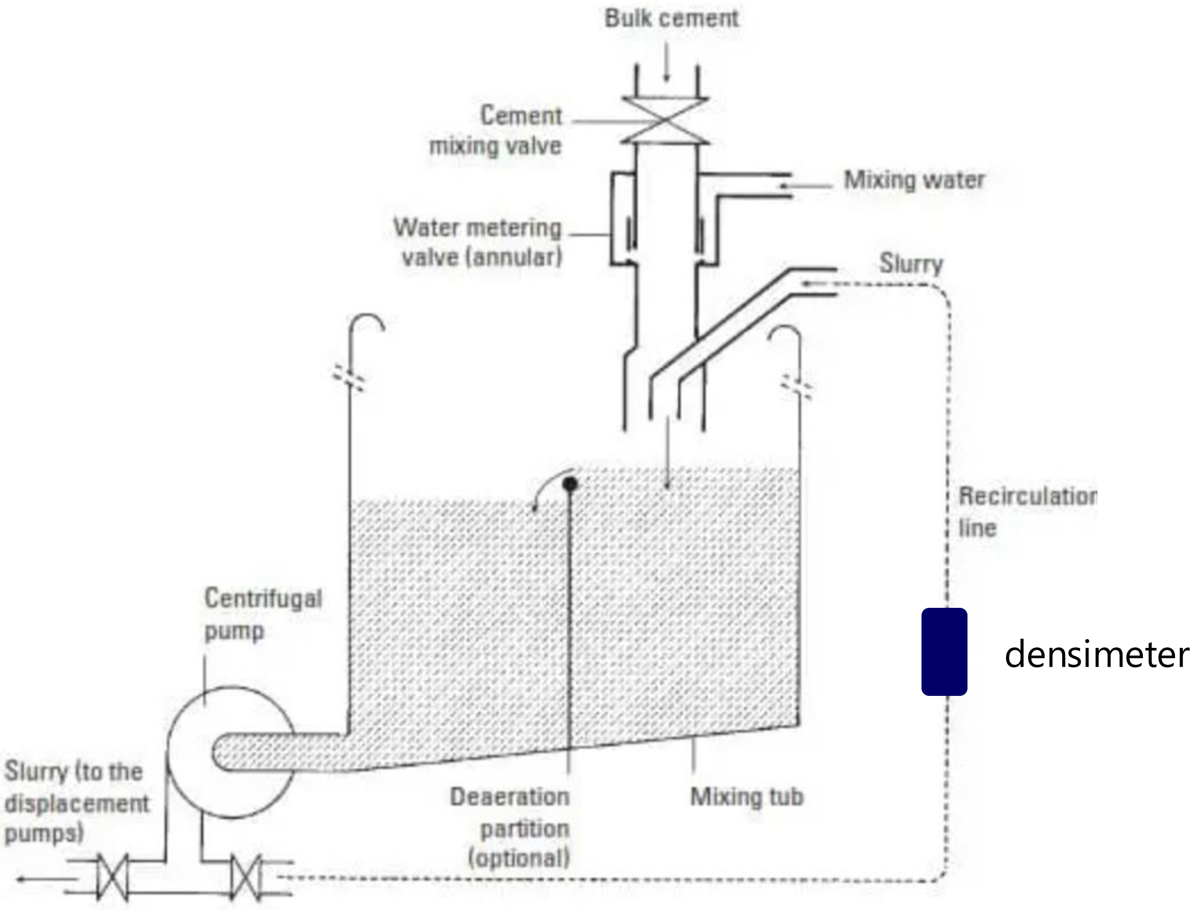
Slurry design / laboratory testing



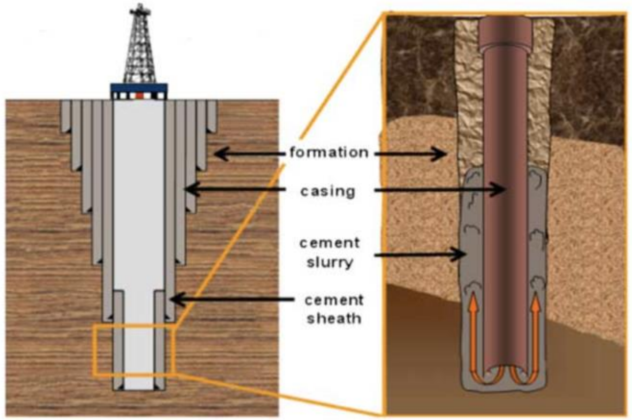
Cement Logistics (pathways)

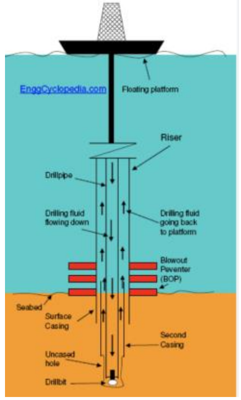


Mixing and pumping of liquid cement slurry



Cement Logistics (pathways)





Cementing Process

- Cementing is a process which includes:
  - Identification and definition of the work to be done;
  - Slurry design and slurry testing (with chemicals);
  - Simulators (specialized softwares);
  - Mixing and pumping through a pumping unit;
  - Cement job evaluation.

- Cement slurry:
  - Result of adding mix water and chemical additives to dry neat or blended cement.

Pumping Unit- offshore

Laboratory Equipment

Silos

Pumping unit- onshore

Monitoring and recording

Downhole tools

Why chemical additives are added to cement?

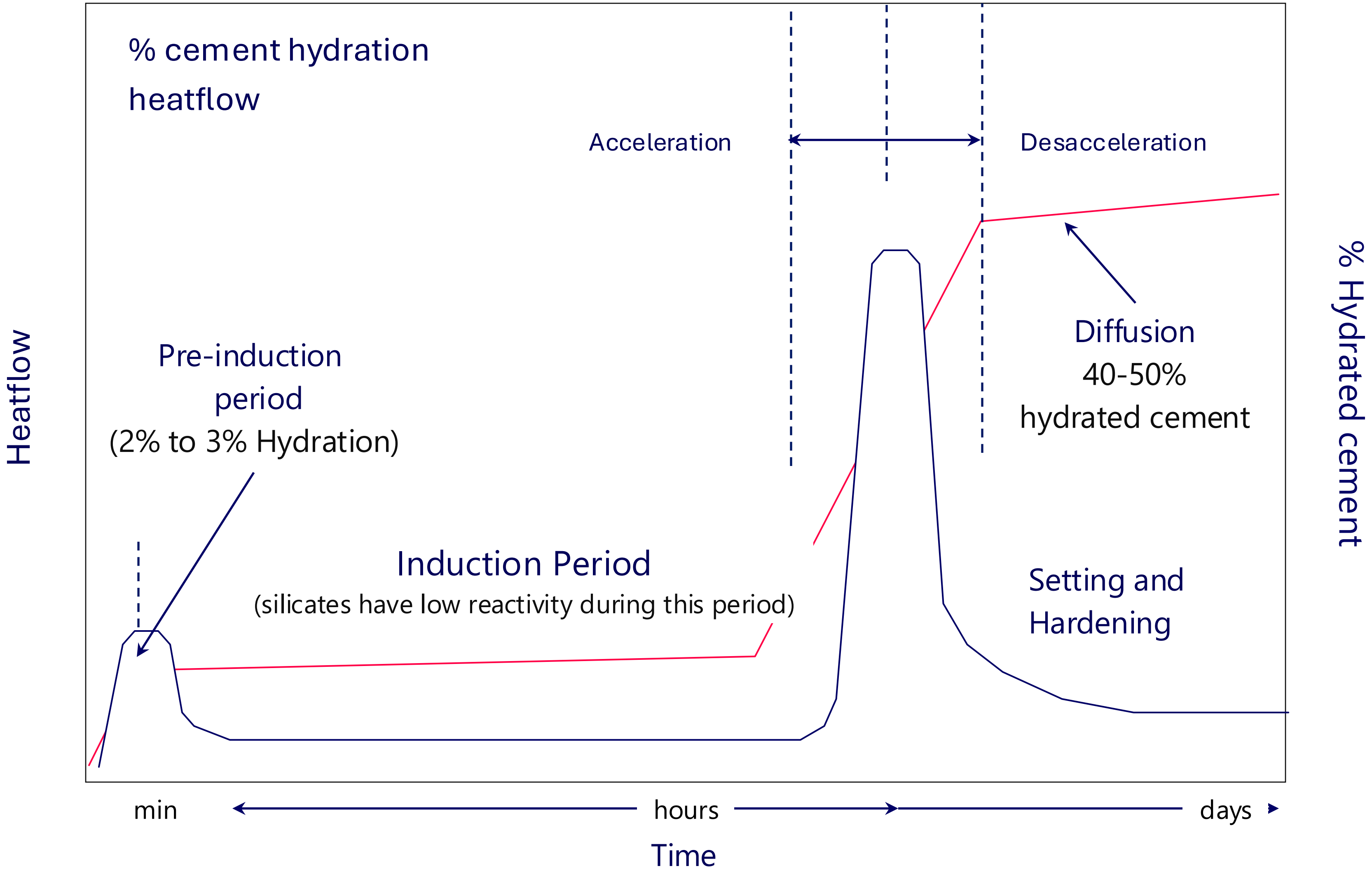
Different goals:

- Fast setting, or slow setting;
- High viscosity - or lower viscosity;
- Compatibility with mud and spacers;
- Use with sea water or industrial water;
- Low cost; gas control; high resistance…;
- High filtrate, or lower filtrate;
- High, low, or no free water.

Different types of work:

- Surface casings – low cost slurry design;
- High temperature and deep critical liners;
- Loss circulation;
- High pressure squeezes;
- Blow out control;
- Well abadonment.

Heatflow during cement hydration



Types of cementing additives

- Accelerators;
- Extenders;
- Retardaders;
- Dispersants;
- Defoamers;
- Loss circulation materials;
- Free water control;
- Densifiers;
- Strength retrogression aditives;
- Fluid loss control;
- Gas influx control...

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Types of cementing additives

What is the usual number of chemical additives in cement slurries placed across hydrocarbon-bearing zones?

1. 1 to 3
2. 3 to 5
3. More than 5

Standardized lab tests (API RP10 B2)

Slurry mixing

Slurry conditioning

Rheology

Fluid loss

Free water

Stability

U.C.A

Compressive strength

Thickening time

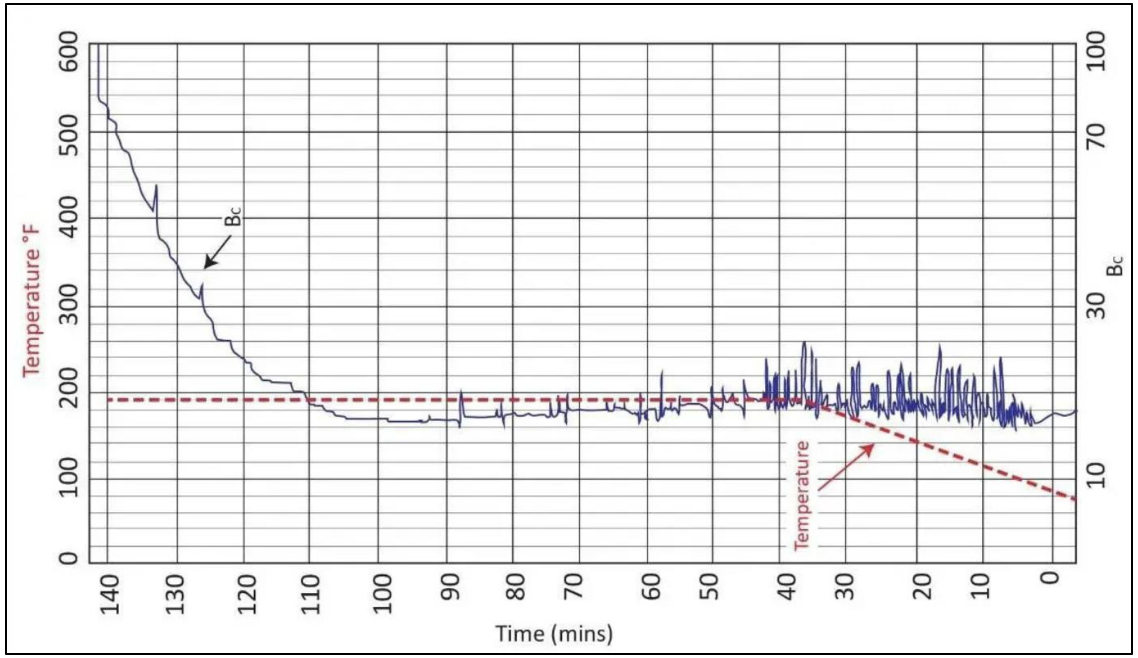
QUIZ TIME

Standardized lab tests (API RP10 B2)

How many cement slurry laboratory tests are typically performed for intermediate casing strings?

1. Up to 3
2. Up to 5
3. Up to 8

Thickening time

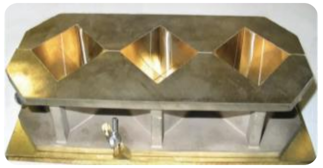


Bc – Bearden Units of Consistency

Compressive strength test (destructive)

Pressurizing
curing chamber
3,000 psi

Cube molds

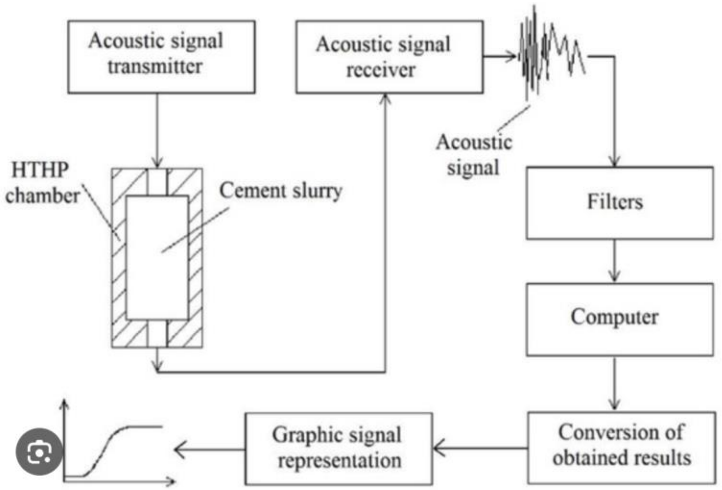


2 in x 2 in x 2 in

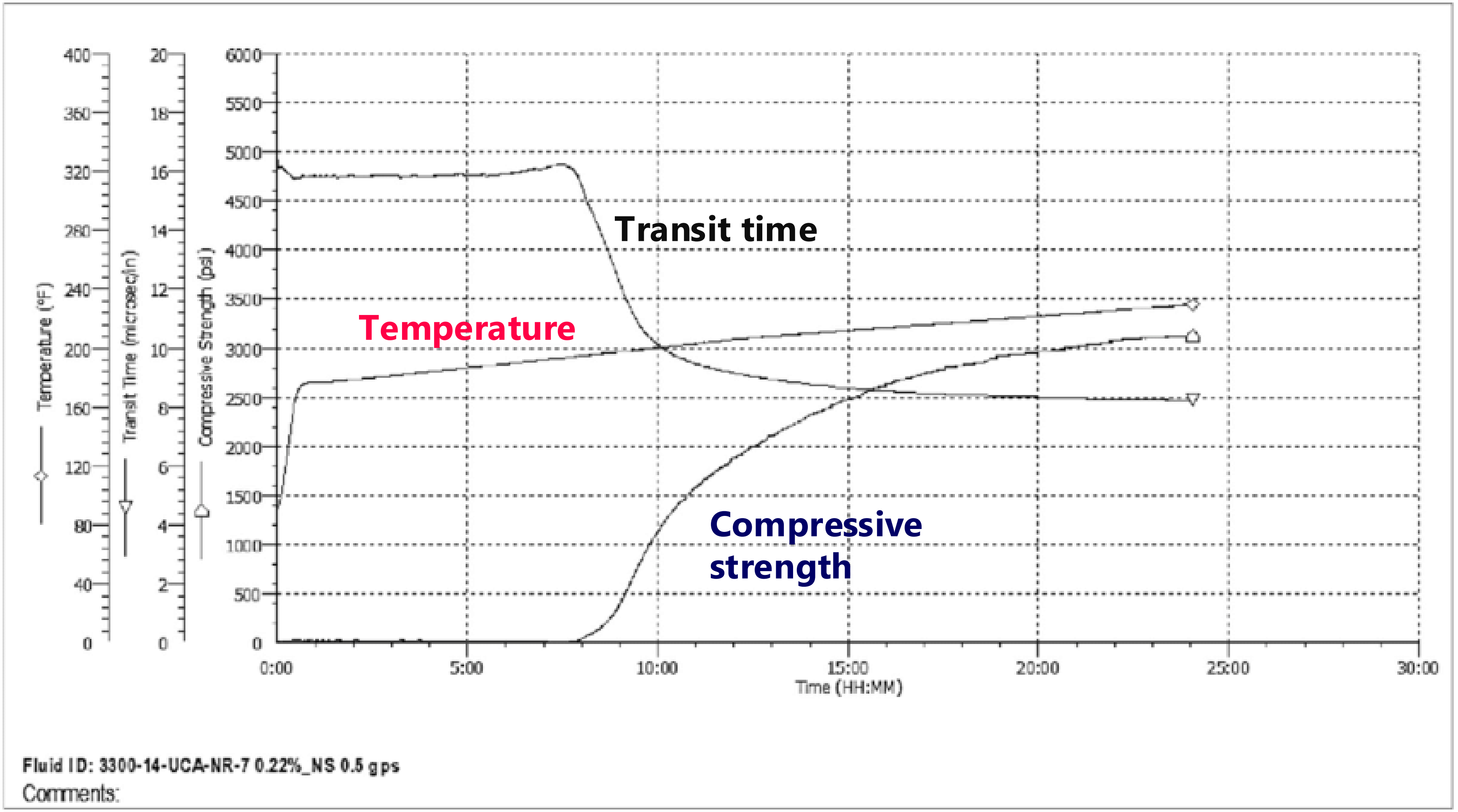
Compressive strength
testing chamber
CS = F (lb)/4 in^2
(in psi)

Compressive strength (non destructive) Ultrasonic Cement Analyzer (UCA)

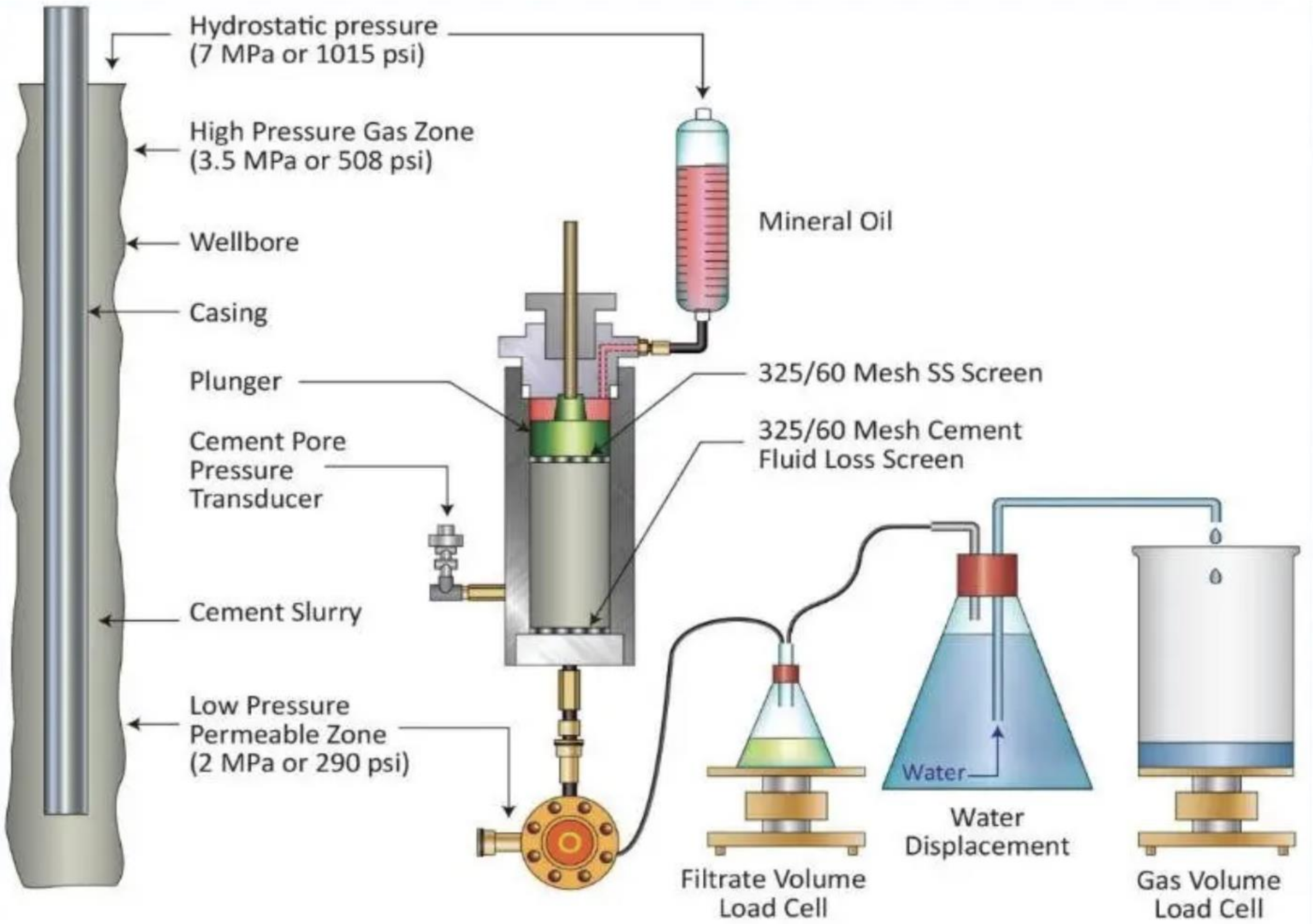
24 hours @ BHTP – measures the ultrasonic transit time passing through the cement slurry and correlates it to compressive strength by means of an algorithm of the control unit.



Compressive strength (non destructive) Ultrasonic Cement Analyzer (UCA)



Gas influx/migration test



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Gas Influx/ migration test

Which set cement properties you consider the most important for preventing gas migration through a cement slurry?

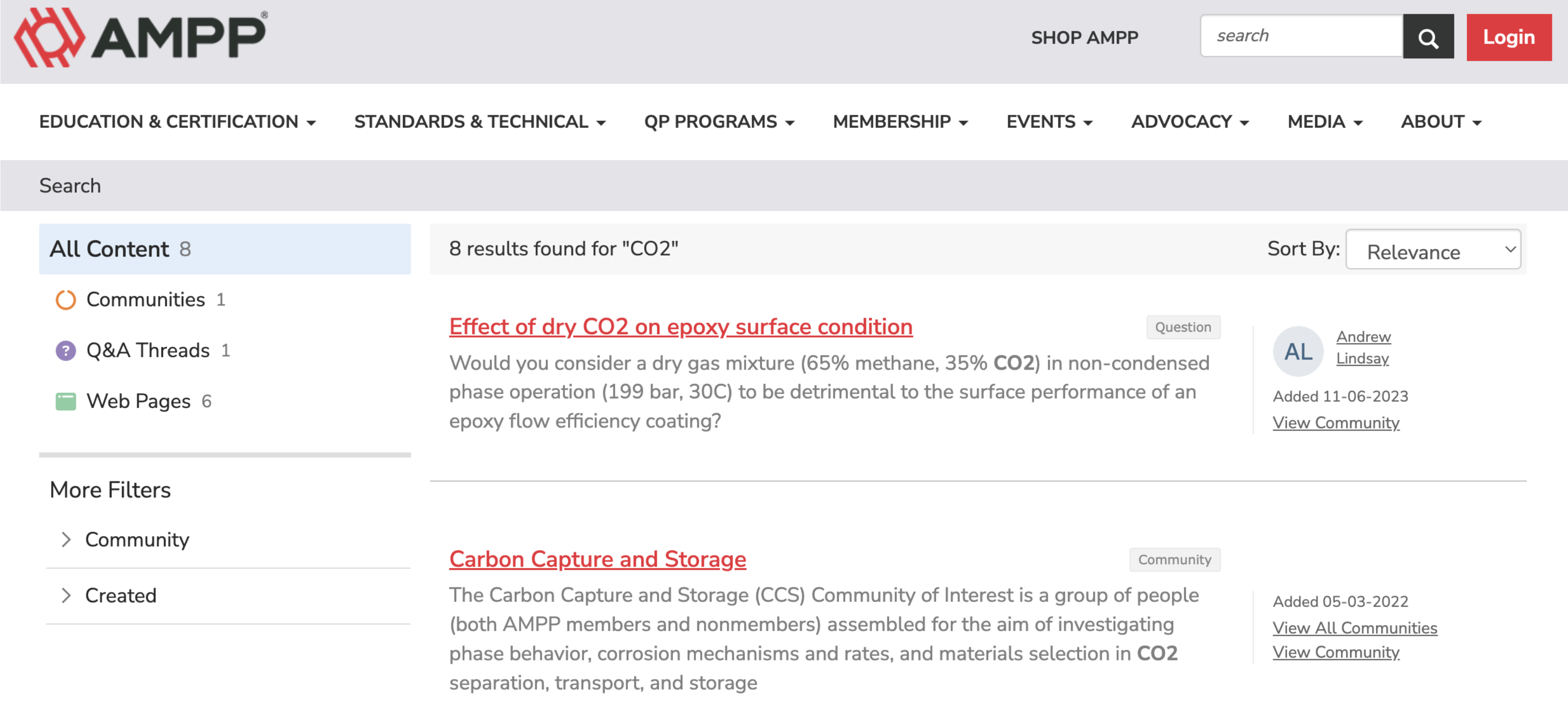
1. Porosity and permeability
2. Quick transition from liquid to solid
3. Density
4. All the above

API testing for CO_2 environments

- There is no API RP protocol for testing cement slurries exposed to CO_2;
- API TR 10TR3 covers, however:
  - General view of CO_2 chemical attack (carbonation process);
  - Discussion of strategies on cement designs exposed to CO_2 environment;
  - Orientation on materials selection (for example, pozzolans, silica, special binding materials);
  - Recommendations and considerations on set cement durability, micro-structure analysis, and required chemical additives.

CO_2 testing (other organizations)

AMPP (Association for Materials Protection and Performance)



CO_2 testing (other organizations)

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Well design for petroleum and natural gas industry systems

SKU: 2424656 | Published by CSA Group | Publication Year 2016 | Reaffirmed in 2021 | 48 pages

Product Details

Preface/Scope | Updates

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1.2
This Standard addresses

a) casing, including casing design for various types of wells, including but not limited to horizontal and directional wells;

b) cementing, including cement design and centralization issues and practices; and

c) wellhead, including design, and assembly.

1.3
This Standard does not apply to

a) completion;

b) operations;

c) abandonment;

d) remedial cementing;

e) interventions;

f) suspensions;

g) competencies;

h) management system requirements;

i) drilling operations;

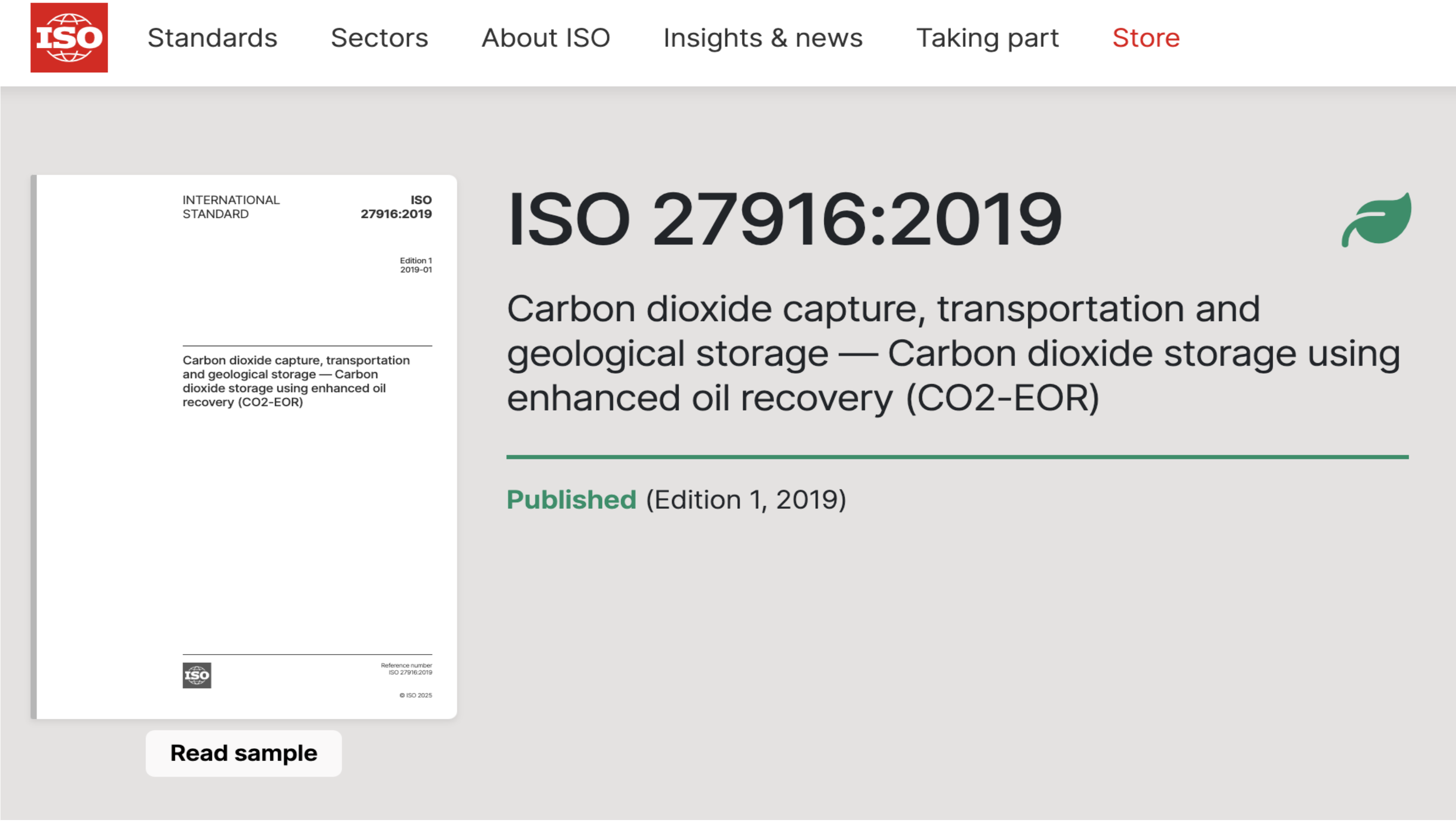
j) emerging technologies;

k) design tools; and

l) offshore and arctic applications.

CO_2 testing (other organizations)

ISO 27916



API testing for H_2S

- There is no API RP or exclusive TR to test cement resistance to H_2S. However, H_2S resistance is indirectly approached through specifications of sulfate resistant cements and general cement testing protocols.

- Service companies, operators and research institutions lean on:
  - Exposure tests in autoclave machines with H_2S rich gas mixtures;
  - Long immersion of set cement in sulfide brines;
  - Petrographic analysis, SEM and XRD of set cement degration;
  - Strength and permeability testing after exposure to H_2S / sulfate brines;
  - Special binding materials (for exemple: pozzolanic mixtures, Classe G + silica fume, latex modified systems...)

API Specifications - Sulfate Resistance

- API cement graduation in respect to sulfate resistance:
  - O (ordinary)
  - MSR (moderate sulfate resistance to SO_4)
  - HSR (high sulfate resistance)

QUIZ TIME

Sulfate Resistance

Where else do we see sulfate attack on set cement?

API Specifications - Sulfate Resistance

H_2SO_4 testing (other organizations)

ASTM C1898-20

- Standard Test Methods For Determining The Chemical Resistance Of Concrete Products To Acid Attack
  - These test methods are intended to evaluate the chemical resistance of cement paste, mortar and concrete materials. This method is loosely based on Test Methods C267, however the solution is more rigorously defined and flexural strength is used. These test methods provide for the determination of changes in the following properties of the test specimens and test medium after exposure of the specimens to the medium:
    - Mass of specimen
    - Appearance of specimen,
    - Appearance of test medium, and
    - Strength of specimens.

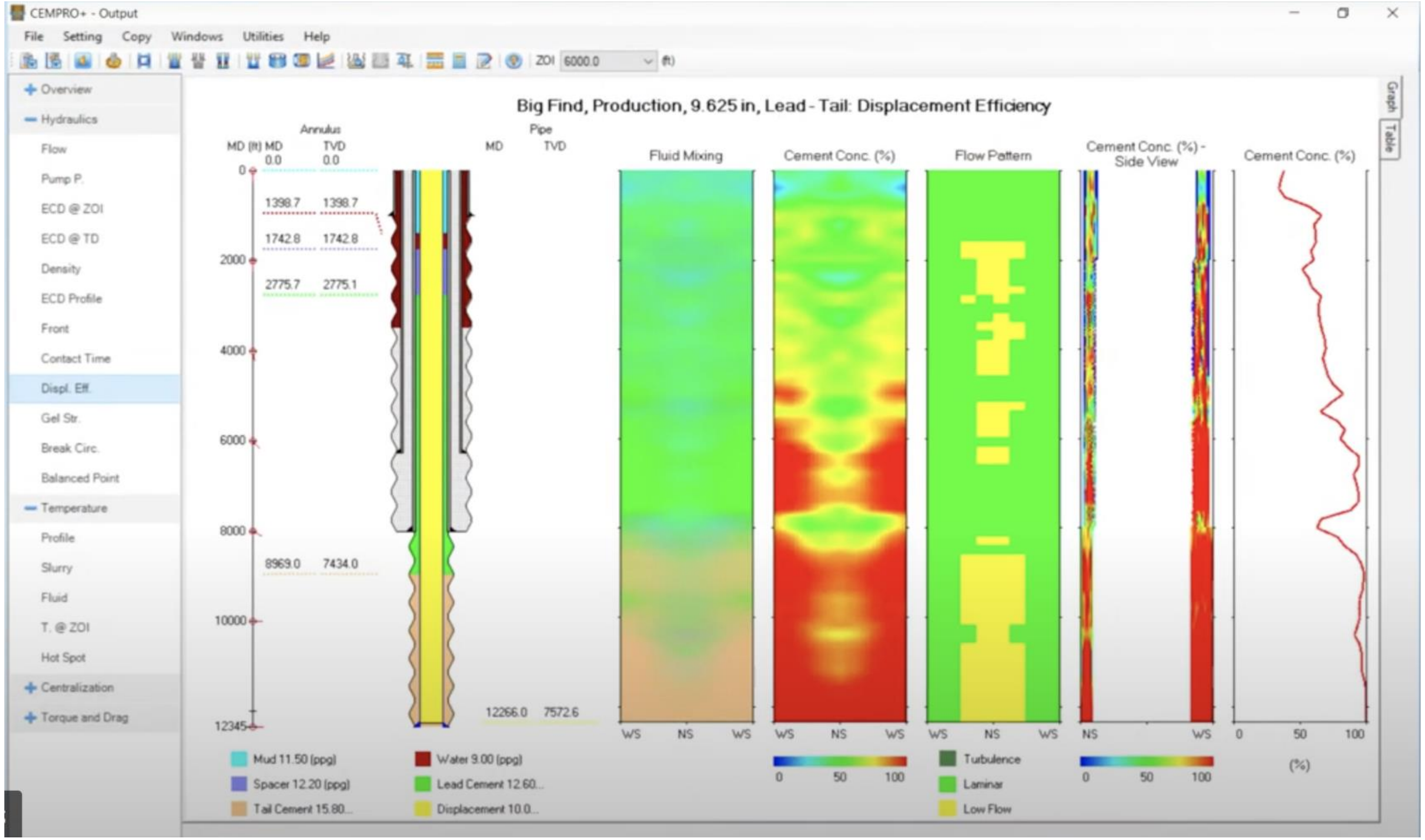

Designation: C1898 – 20

Standard Test Methods for
Determining the Chemical Resistance of Concrete Products
to Acid Attack[1]

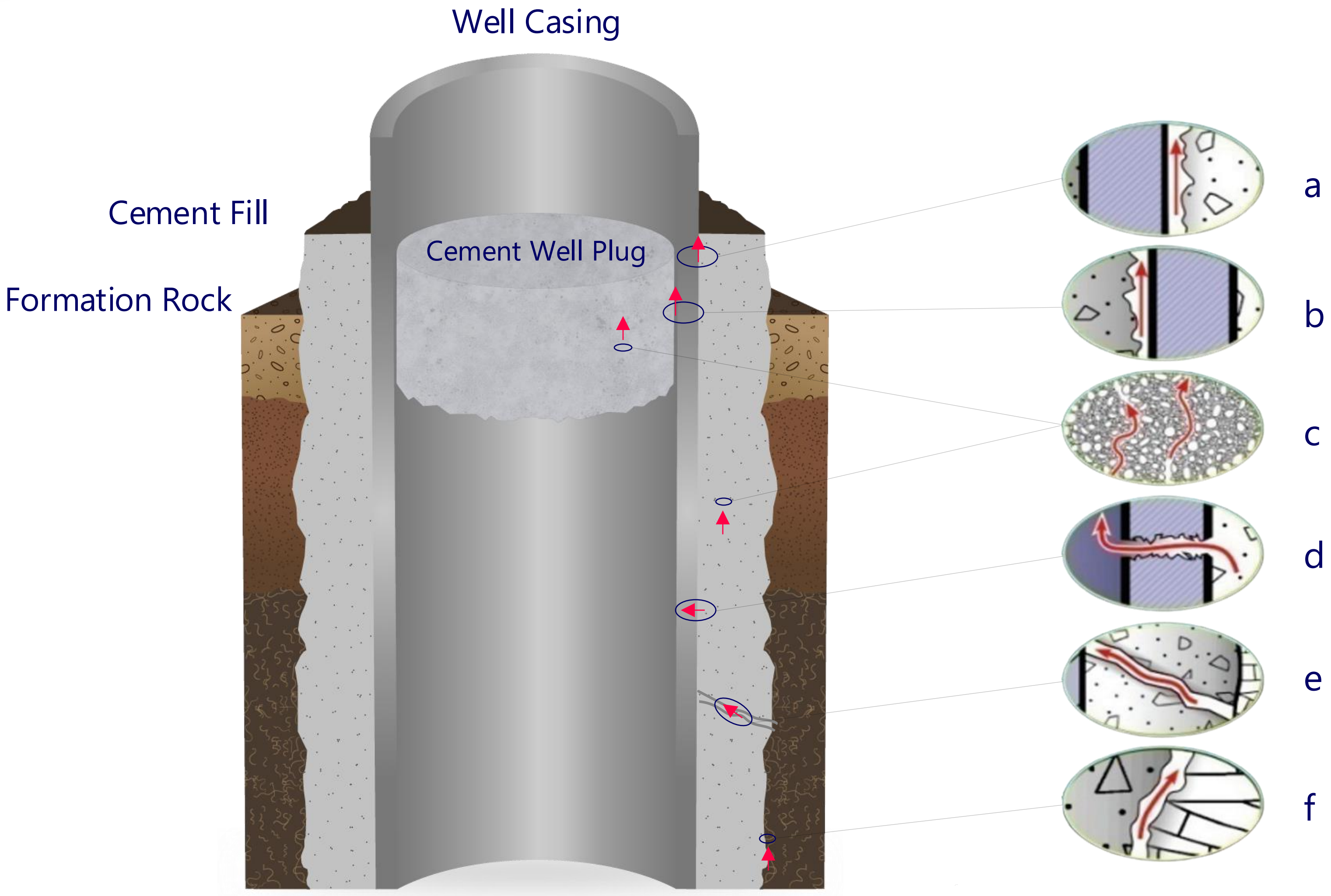
Well Cementing Simulators

- Sources:
  - Service companies;
  - Independent specialized software companies.

Well Cementing Simulators

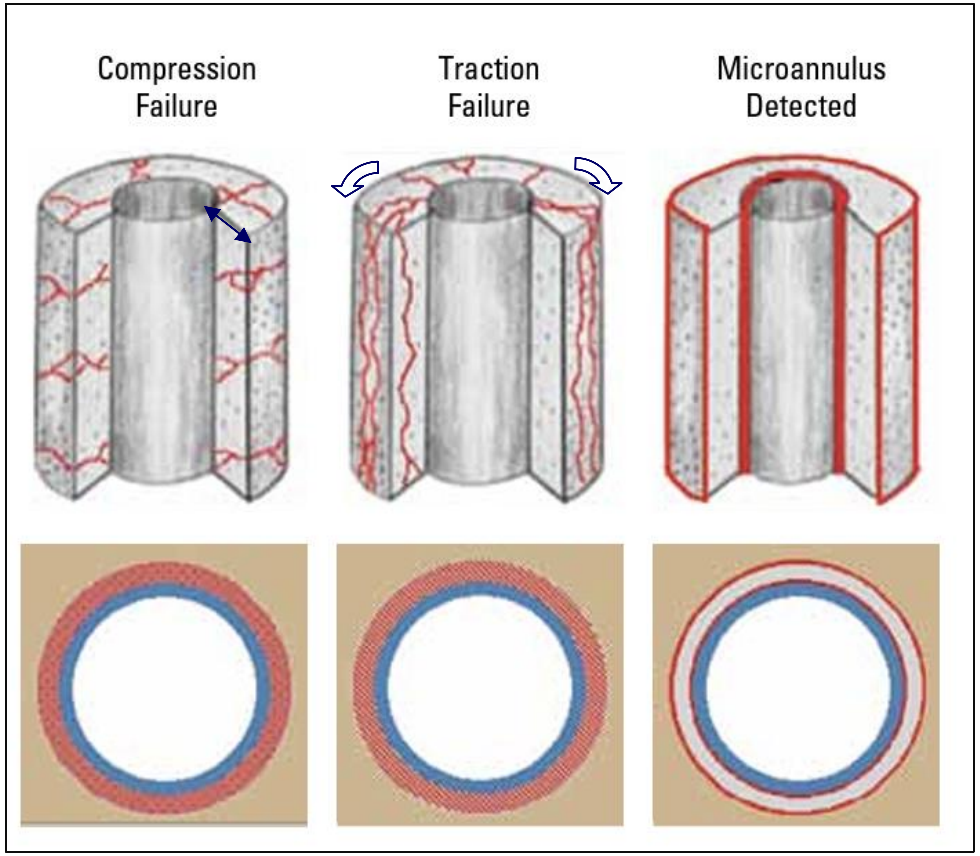


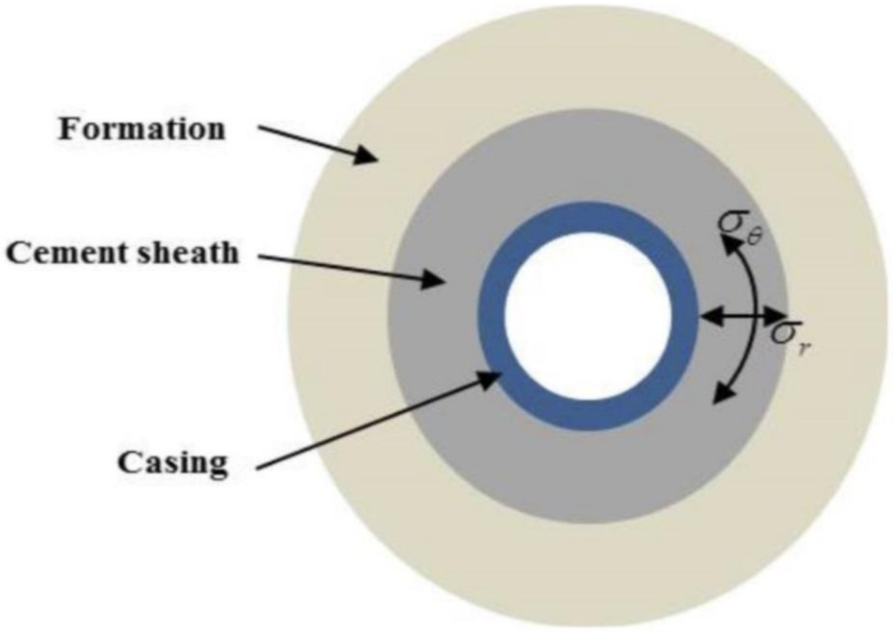
Potential Leakage Pathways



Gasda et al., 2004 and 2005

Factors Impacting Cement Integrity



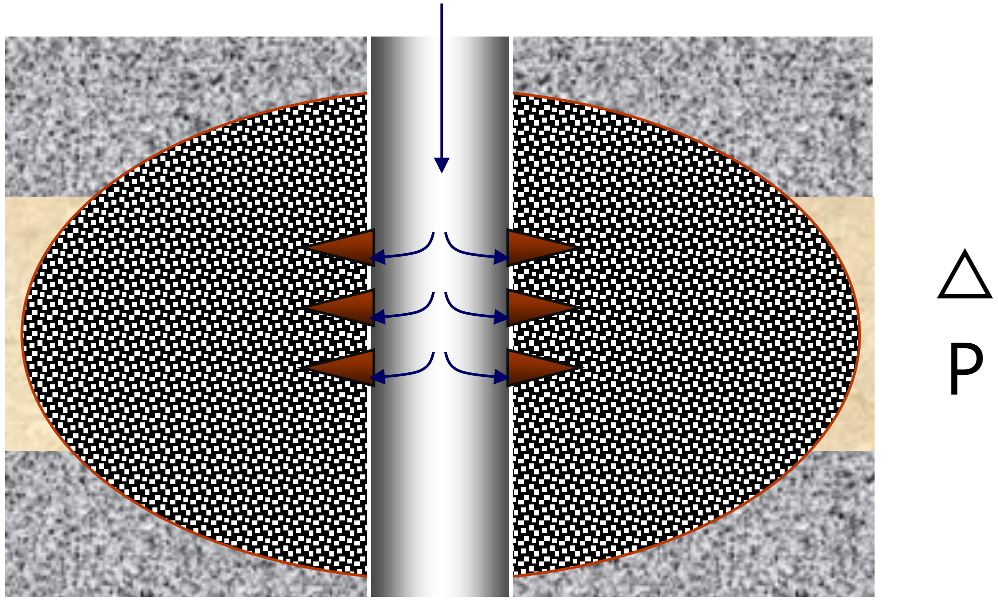


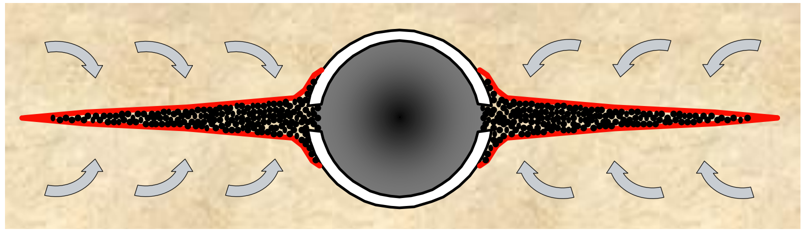
Hydraulic Fracturing

- High rate and high pressure pumping, injecting frac fluids into the formation, creating fractures...

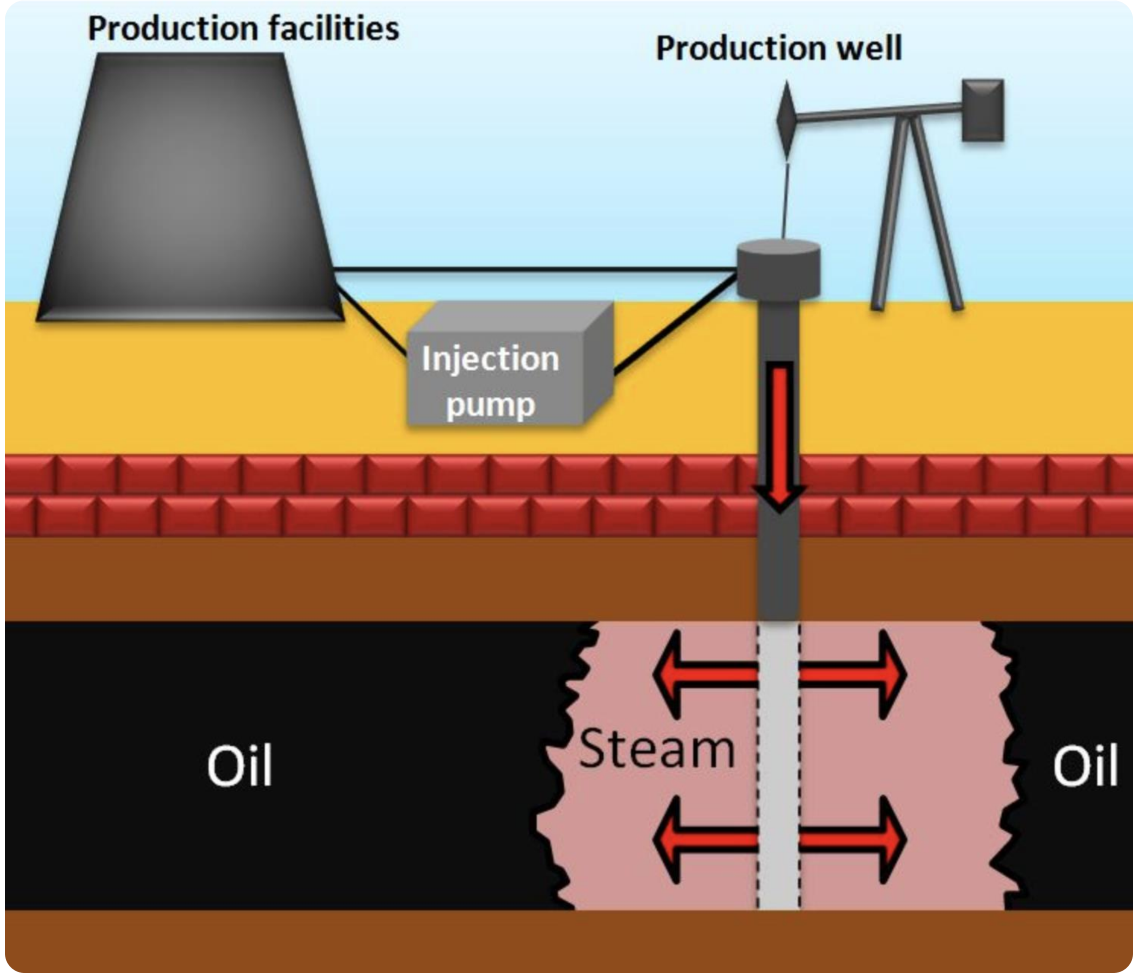
- After the fractures are created, sustaining agents, also called proppants, are pumped in...

- The fracture is filled in by proppants, at the end of the pumping, in order to keep it open and to facilitate fluids from the reservoir to the well.





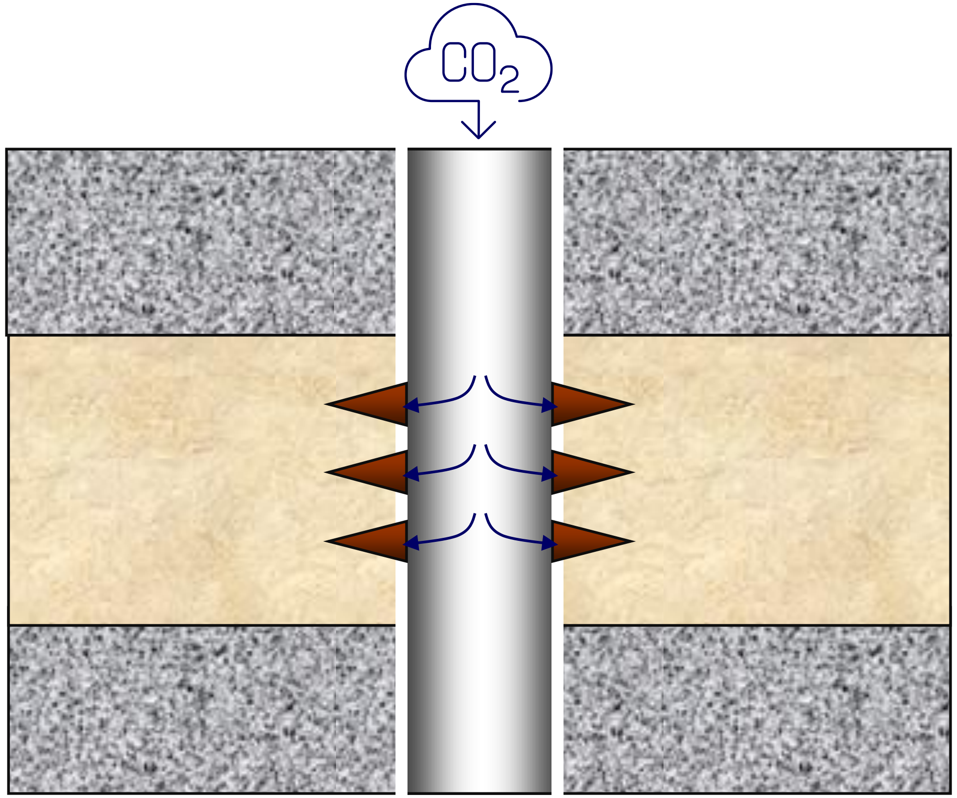
Steam Injection in Enhanced Oil Recovery



ΔT

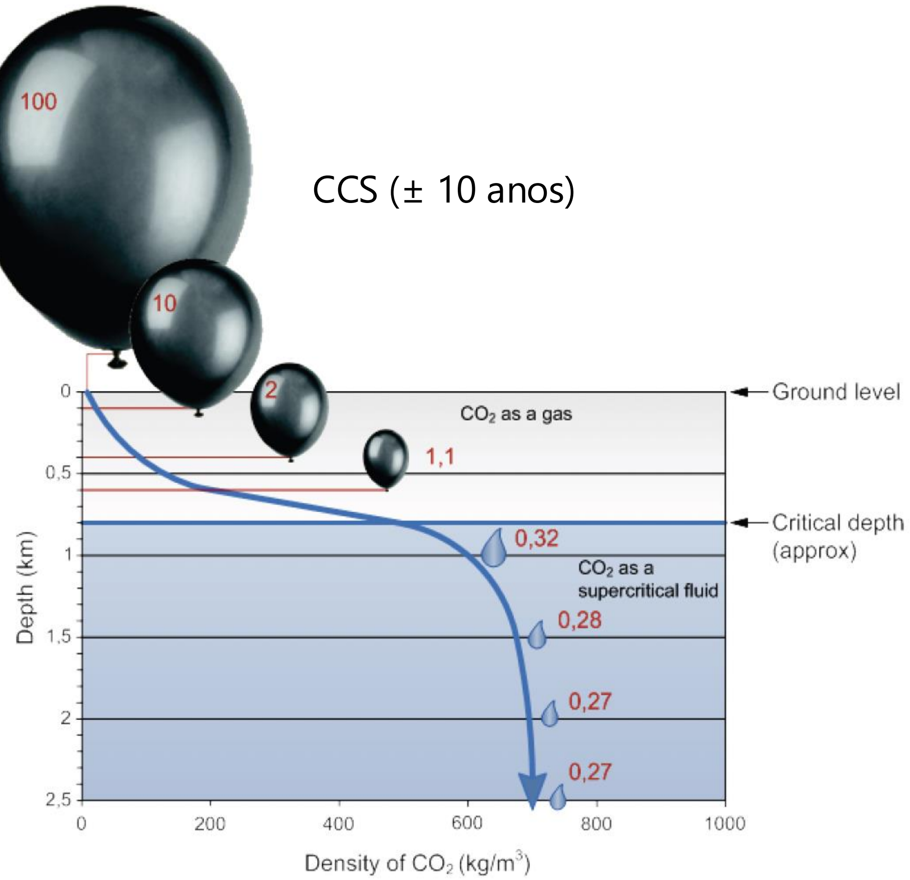
CO_2 Injection (EOR)

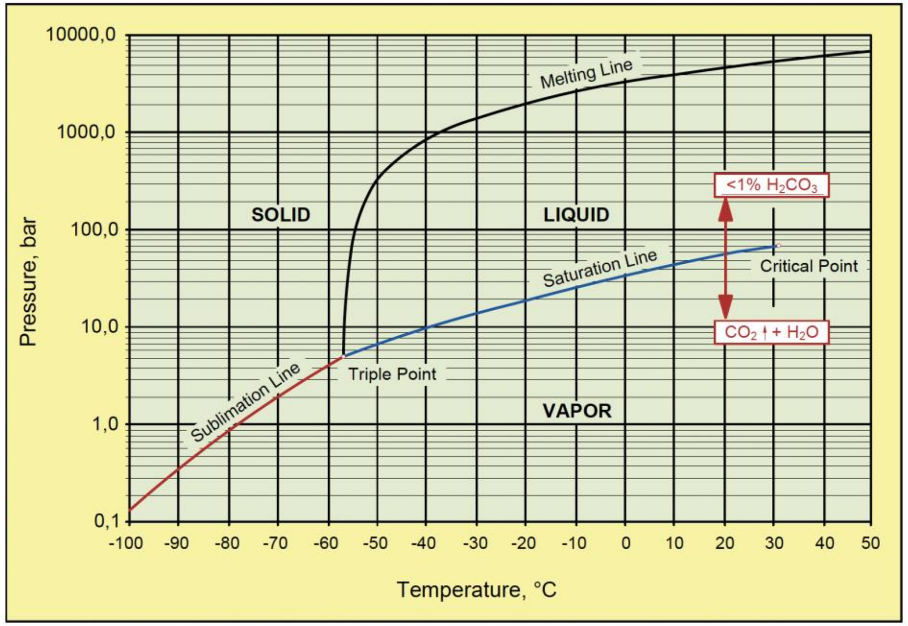
- CO_2 injection is a proven EOR technique (± 45 years);
- Injected CO_2 reduces oil viscosity and interfacial tension;
- Under high pressure, CO_2 becomes miscible with oil, improving recovery;
- It helps to keep reservoir pressure and improves oil sweep efficiency;
- Recovery increases by 10 to 20% or more in comparison with water injection;
- Captured industrial CO_2 can be reutilized, contributing to carbon management;
- Importance to set cement: wells should keep integrity when exposed to CO_2.



CO_2 Injection (EOR)

CCS (± 10 anos)

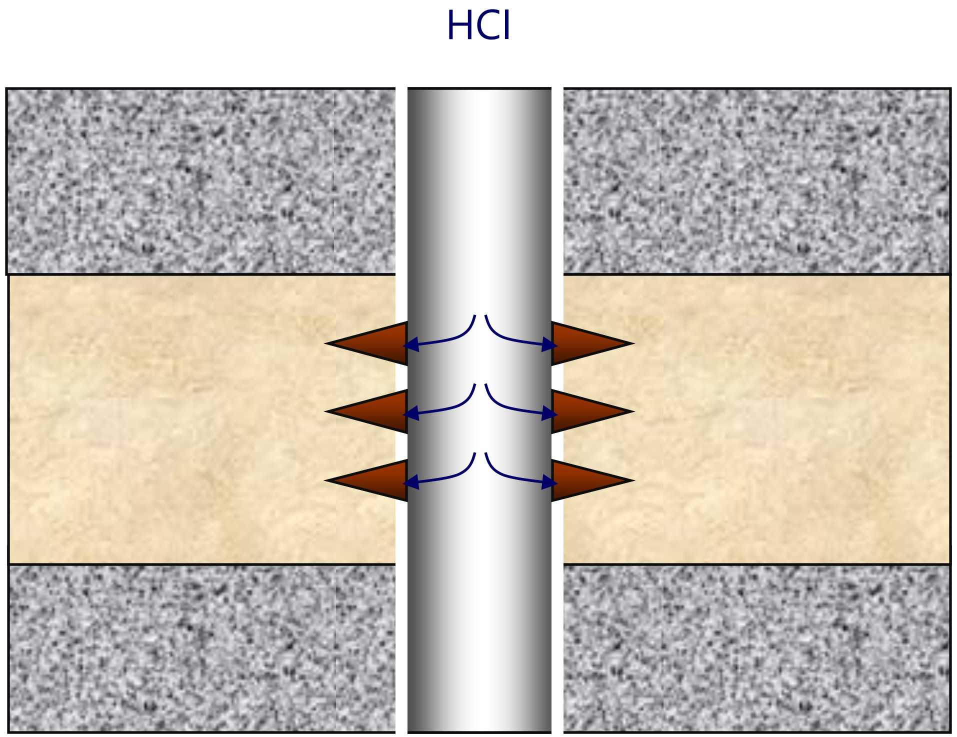




IEA, 2008

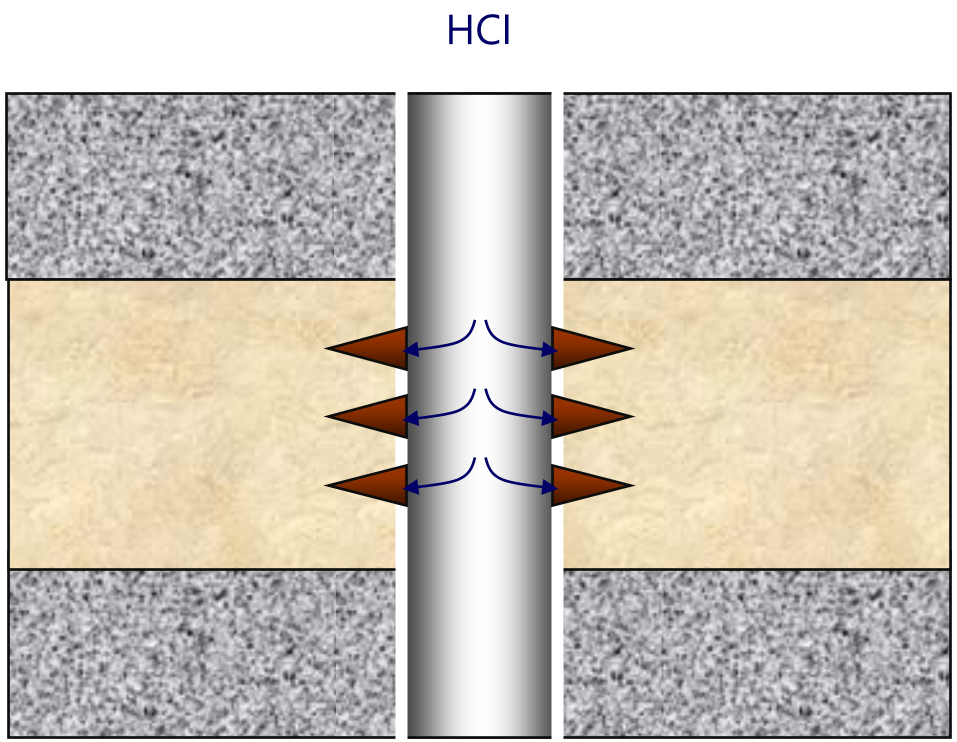
HCl Injection (Stimulation)

- Acid stimulation fluids, especially hydrochloric acid (HCl), can cause serious damage to set cement if they come into contact with it. Here's what happens:
  - Dissolution of Cement Phases
    - HCl aggressively reacts with $Ca(OH)_2$ and other cement hydrates, such as calcium silicate hydrate (C–S–H), which are key to the strength of set cement.
    - This leads to decalcification, weakening the cement structure.
  - Increase in Porosity and Permeability
    - As acid dissolves cement compounds, it opens up the cement matrix, increasing porosity and permeability.
    - This compromises the sealing capability of the cement, potentially allowing fluid migration along the annulus.



HCl Injection (Stimulation)

- Strength Loss
  - Progressive acid attack leads to loss of compressive strength, making the cement sheath unable to withstand pressure or mechanical loads.
- Zonal Isolation Failure
  - Damaged cement can lead to zonal isolation failure, resulting in crossflow between formation layers, gas migration, or sustained casing pressure (SCP).
- Risk of Well Integrity Compromise
  - In severe cases, acid-induced degradation of cement jeopardizes overall well integrity, requiring expensive remediation or re-cementing.



QUIZ TIME

HCl Injection (Stimulation)

In which likely scenario below do we have acid attacking set cement?

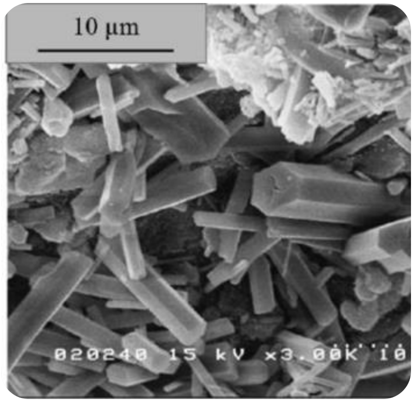
1. Raining over concrete bridges
2. Fresh water over cemented floor
3. Paint over concrete walls

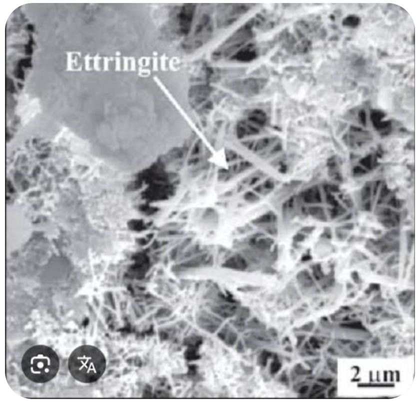
What is set cement?

Ettringite is formed during the initial hydration of cement when C_3A reacts with gypsum ($CaSO_4.2H_2O$) in the presence of water:
$Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$

It controls thickening time and cement setting time.

Compound	Chemical formula	Abbreviation	Typical Mass (%)	Contribution on performance
Tricalcium aluminate	$3CaO{\cdot}Al_2O_3$	C_3A	5 -12%	Durability and early setting





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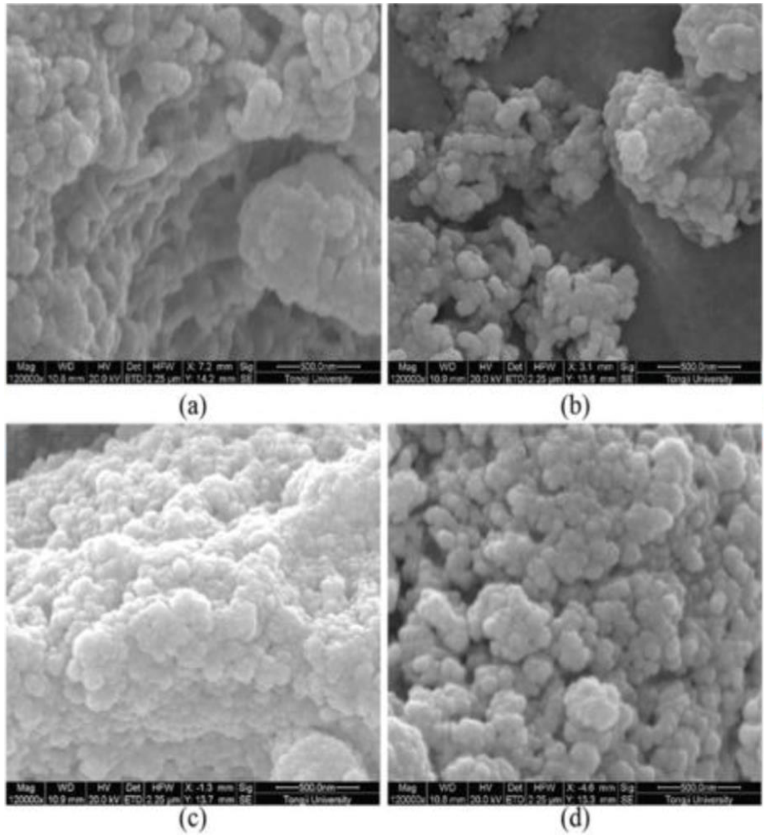
What is set cement?



C-S-H (Calcium Silicate Hydrate) is the main phase which keeps the cement particles binded together, providing cohesion and resistance. It does not have a defined chemical formula and is amorphous. It is formed from the hydration of Portland cement silicate phases:

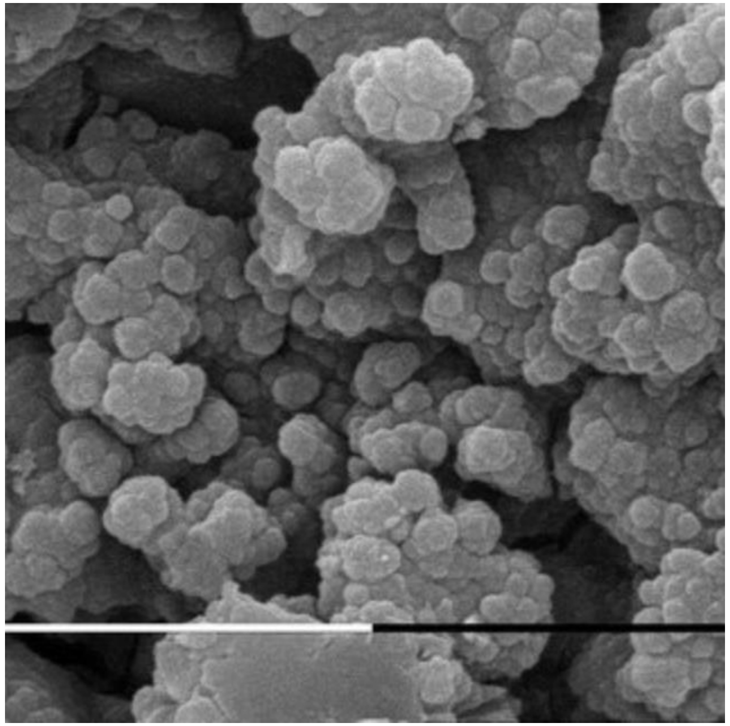
$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3\,Ca(OH)_2$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + Ca(OH)_2$$

It controls cement permeability (gelled structure which fills the pore spaces), besides resisting to chemical attacks, and improve cement durability over cement long term life.

Compound	**Abbreviation**	**Chemical Formula**	**Typical Mass** (%)	**Contribution on performance**
Tricalcium silicate (Alite)	C_3S	$3CaO{\cdot}SiO_2$	45–60%	Durability and total resistance
Dicalcium silicate (Belite)	C_2S	$2CaO{\cdot}SiO_2$	15–30%	Long term durability

What is set cement?



$Ca(OH)_2$ (Calcium Hydroxide) is byproduct of Portland cement silicate phases hydration:

$2C_3S + 6H \rightarrow C_3S_2H_3 + 3\ Ca(OH)_2$

$2C_2S + 4H \rightarrow C_3S_2H_3 + Ca(OH)_2$

It is also called hydrated lime or portlandite.

It provides alcalinity (high pH) to the pore solution, helping metal protection against corrosion in harmful environments. It is also one of the main reactants to CO_2 attack (carbonation reaction).

Compound	**Abbreviation**	**Chemical Formula**	**Typical Mass** (%)	**Contribution on performance**
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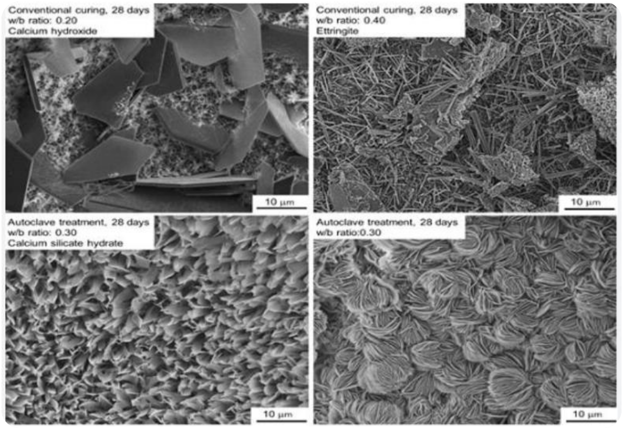
What is set cement?

The main products generated by the cement hydration process are the Calcium Silicate Hydrate gel – CSH – and the Calcium Hydroxide – $Ca(OH)_2$.

CSH is semi-amorphous material, similar to a gel, which make up approximately 70% in weight of hydrated cement and is the main particles binder.

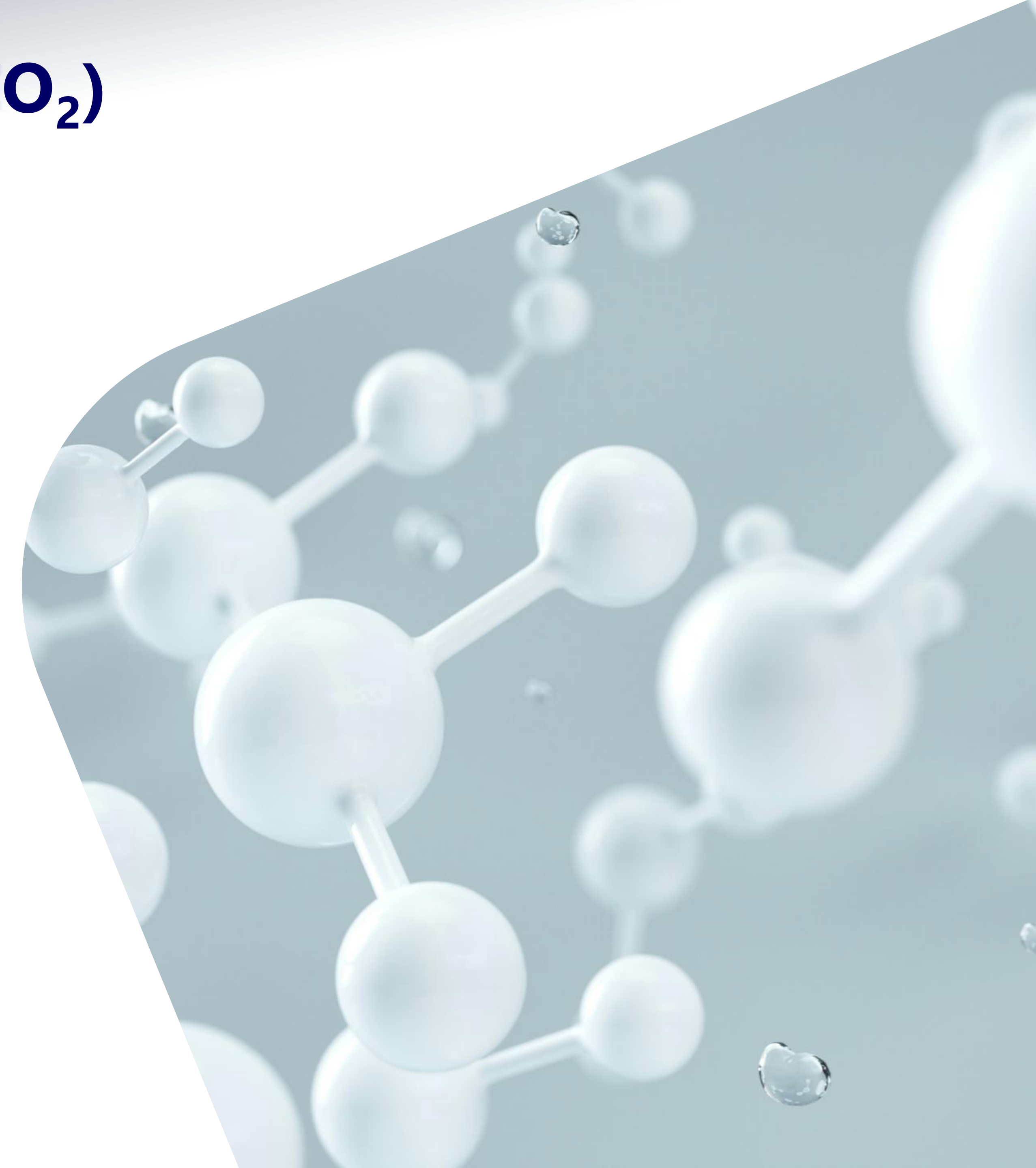
$Ca(OH)_2$ is crystalline and make up approximately 15 to 20% in weight of hydrated cement.



Nelson e Guillot, 2006)

Related Chemical Reactions (CO_2)

1. $CO_2 + H_2O \rightarrow H_2CO_3$ (carbonic acid)
2. $H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$
3. C-S-H and/or crystalline phases + $H_2CO_3 \rightarrow CaCO_3 + SiO_2$ (gel) + H_2O
4. $CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$



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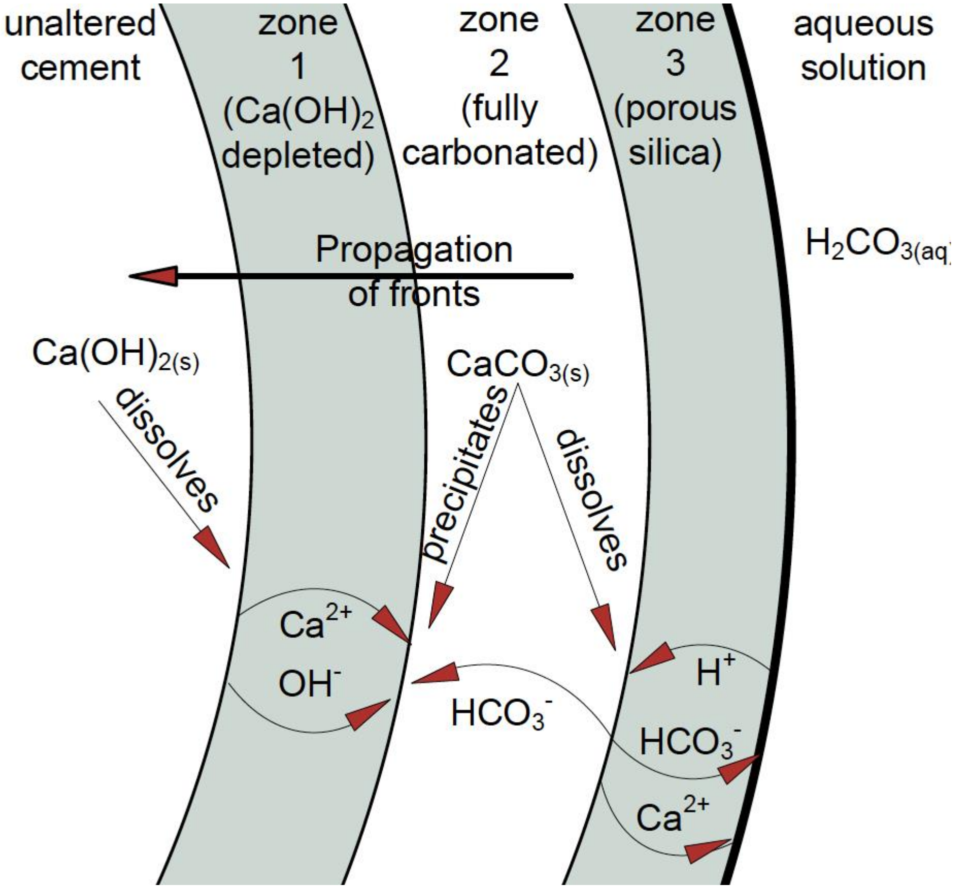
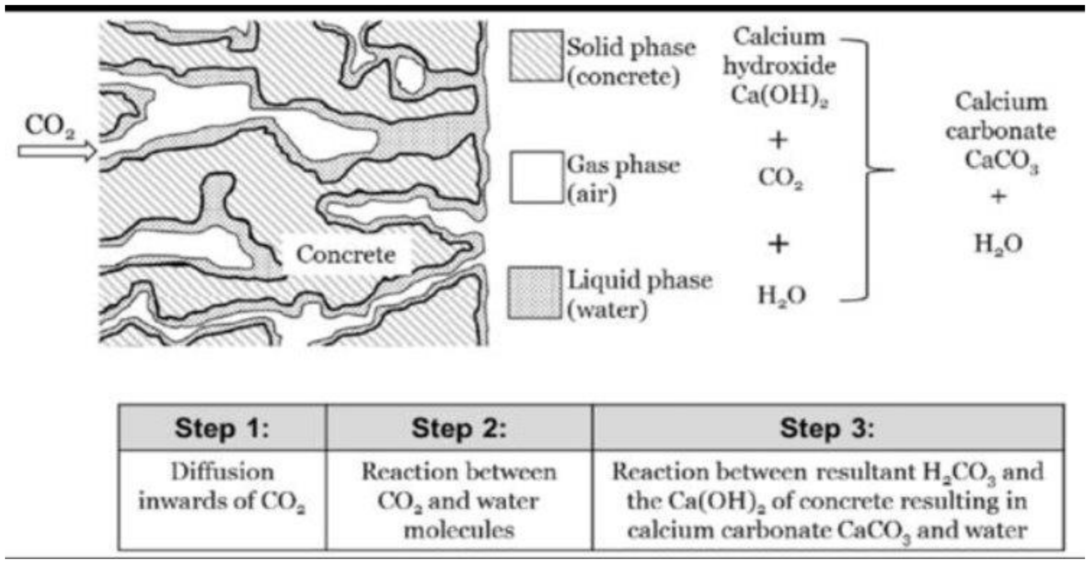
Related Chemical Reactions (CO_2)



The dissolution and calcium migration and formation of distinct zones in the set cement.

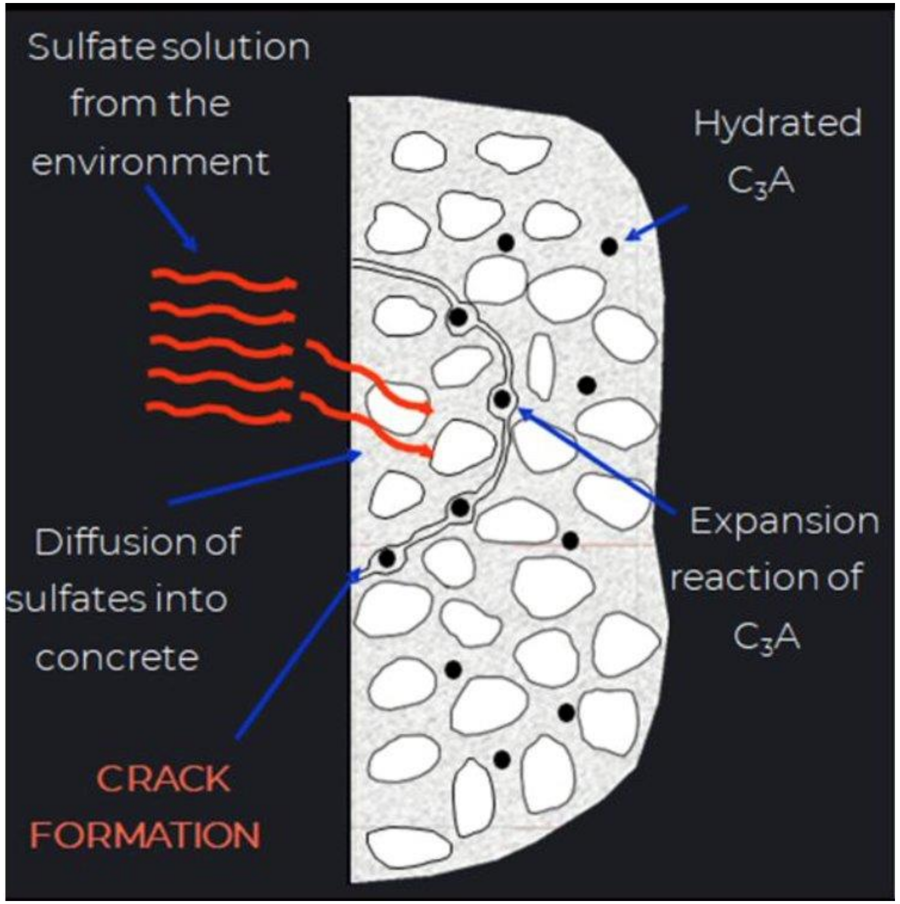


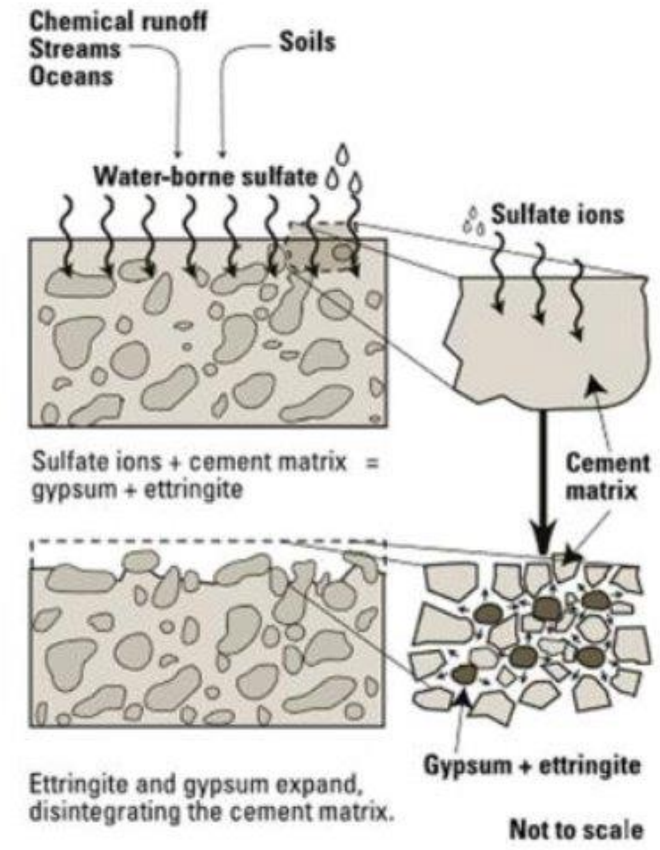
(Kutchko et al., 2007)

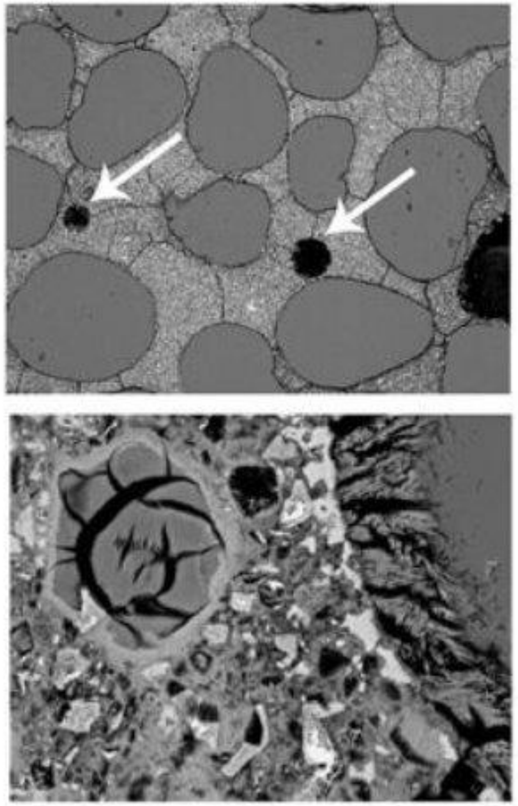
Related Chemical Reactions (H_2S)

1. $H_2S + Ca(OH)_2 \rightarrow CaS + 2H_2O$
2. $CaS + 2H_2O + CO_2 \rightarrow CaCO_3 + H_2S\uparrow$
3. Monosulfates react with C_3A, forming expansive crystals:
    - Ettringite:
      $C_3A + 3(CaSO_4{\cdot}2H_2O) + 26H_2O \rightarrow C_6A\check{S}_3H_{32}$
      $(3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O)$
    - Gypsum ($CaSO_4{\cdot}2H_2O$):
      Can also form if excess sulfate reacts with calcium hydroxide (portlandite)

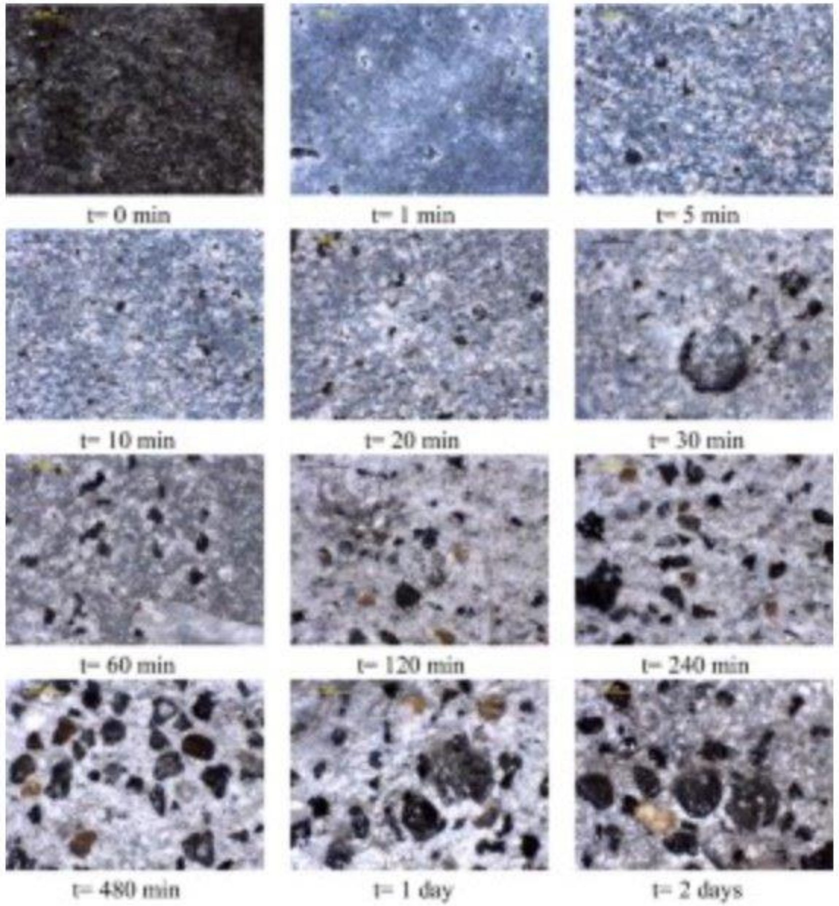
Related Chemical Reactions (H_2S)

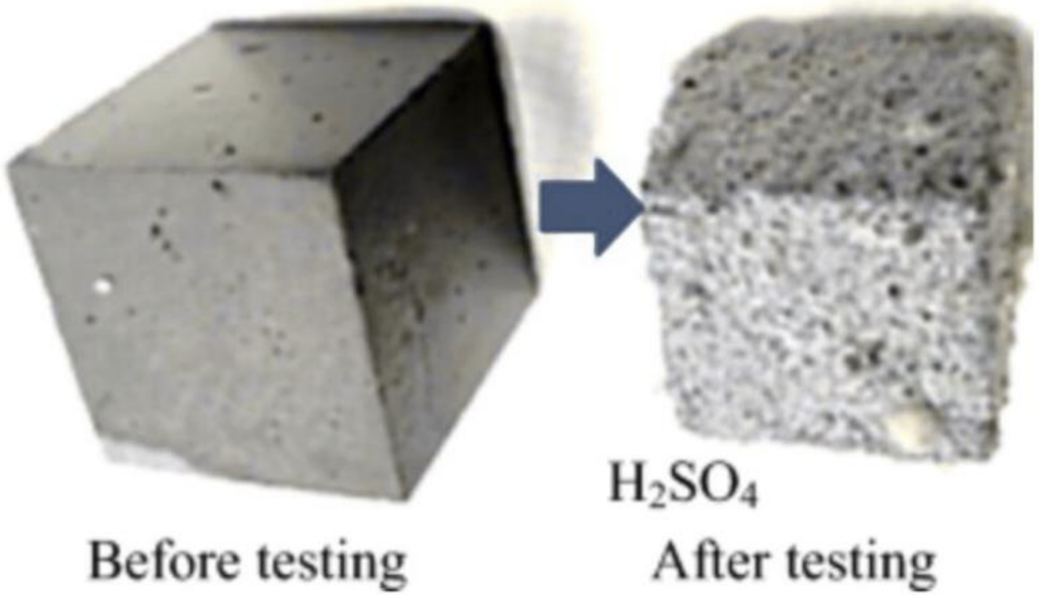






Related Chemical Reactions (H_2S)



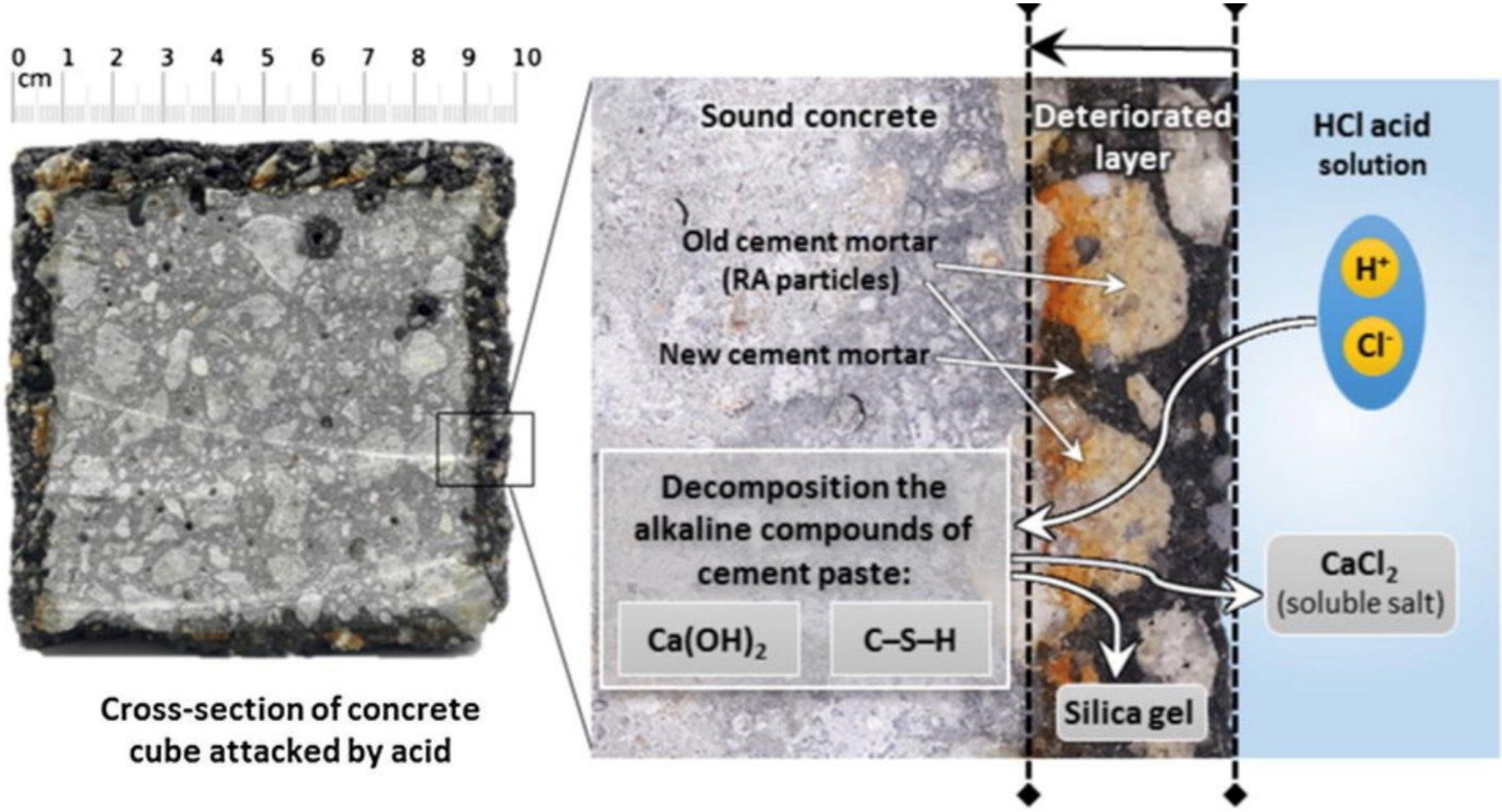


Related Chemical Reactions (HCL)

1. $2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$
2. $CSH + 2HCl \rightarrow SiO_2 . xH_2O$ (gel) $+ CaCl_2$
3. Reaction with Ettringite :

   $C_6A\check{S}_3H_{32} + 12HCl \rightarrow AlCl_3 + CaCl_2 +$ byproducts
4. $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2\uparrow + H_2O$

Related Chemical Reactions (HCL)



Mechanisms of Cement Degradation

Dissolution:

Loss of $Ca(OH)_2$ reduces alcalinity.

Precipitation:

Formation of secondary minerals such as $CaCO_3$ and CaS.

Structural alterations in high temperature:

Increase of porosity and micro fissures reduce mechanical resistance.

Effect of Temperature in Corrosion

Temperature:

- Temperature increase accelerate chemical reactions;
- Corrosion at 90°C is higher than at 50°C, under the same time exposure.

Time:

- The longer the exposure time, the greater the corrosion penetration;
- The corrosion depth grows rapidly in the first few days and tends to stabilize over time.

Effect of Corrosion on Compressive Strength

1

Corrosion reduces the mechanical resistance of set cement.

2

Increase of porosity and formation of microcracks compromise the structural integrity of set cement.

Effect of High Temperature (>110°C) on Mechanical Properties of Set Cement

1

$C_3S_2H_3$ becomes unstable and transforms itself in a hydrated C_2S of low resistance.

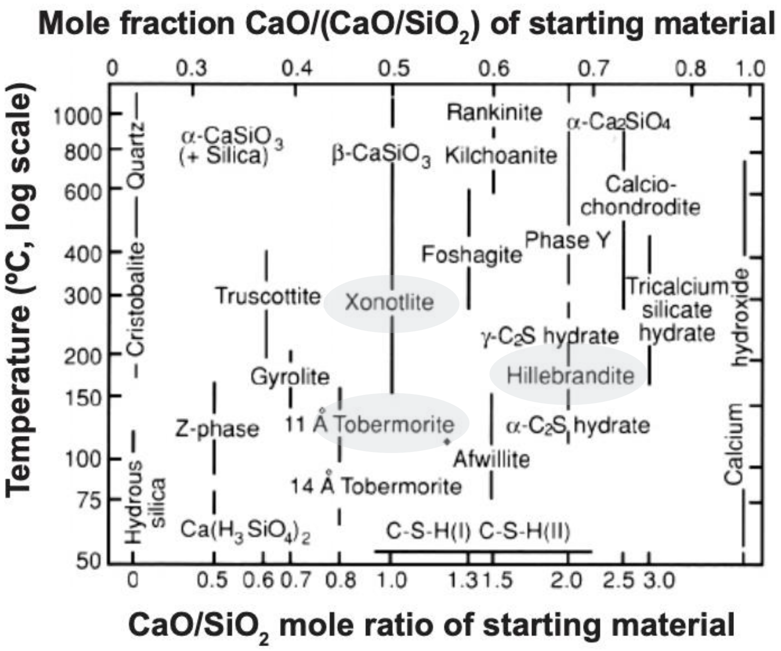
2

The crystallization degree of the hydrated byproducts is limited, and the dehydration of crystals further deteriorate the compressive strength of cement.

3

Increase of porosity and formation of microcracks compromise the structural integrity of set cement.

Effect of High Temperature (>110°C) on Mechanical Properties of Set Cement



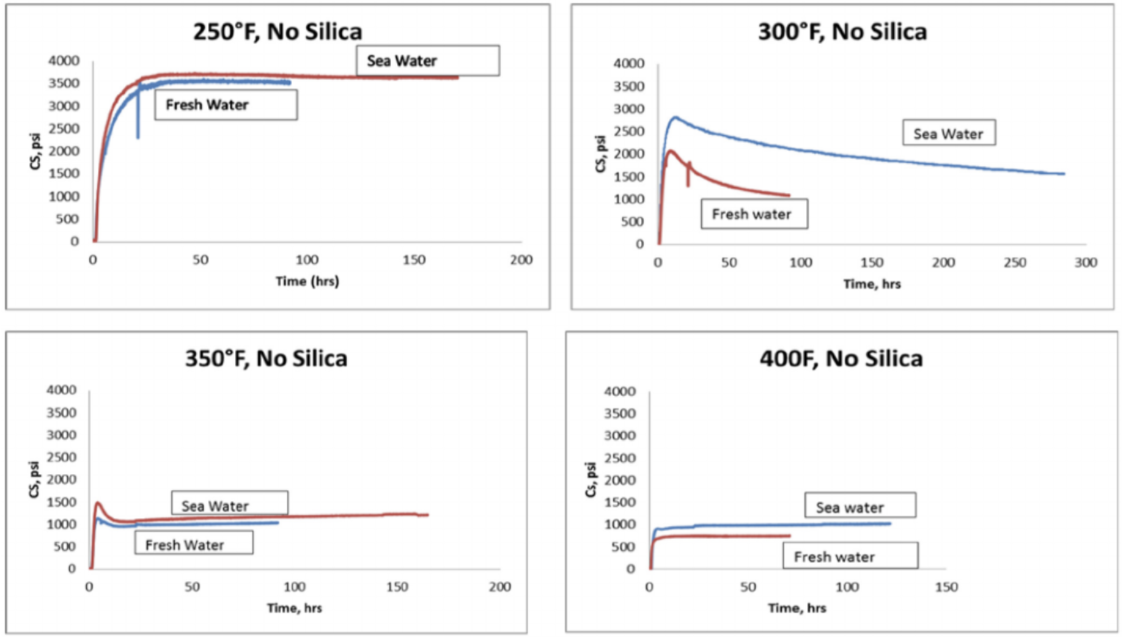
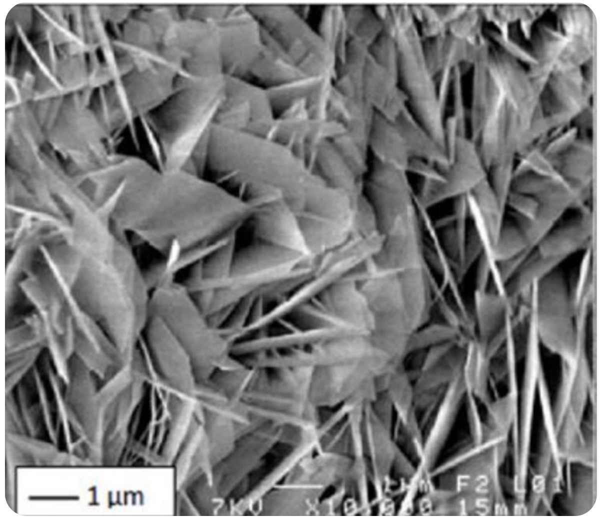


Figure 3—Early Strength development patterns for fresh and sea water formulations without silica flour

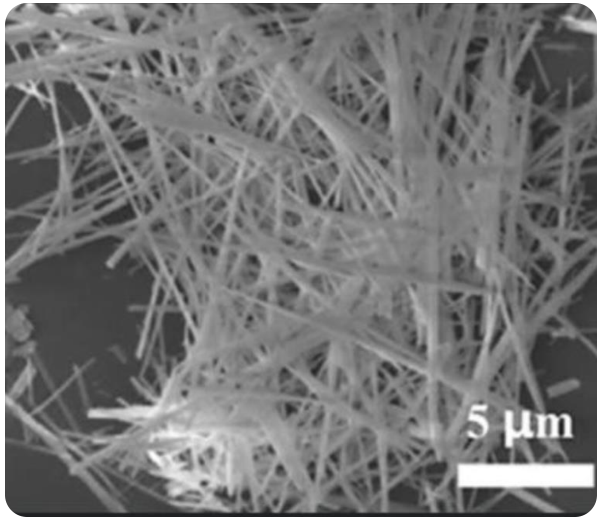
Figure 1: Phase changes in Portland cement submitted to elevated temperatures.

Effect of High Temperature (>110°C) on Mechanical Properties of Set Cement

Tobermorite



Xonotlite



Mitigation Strategies

- Selection of corrosion resistance materials, such as pozzolanic cement and special anti-corrosion additives;
- Designs with more adequate materials for the maintenance of long term cement strength in high temperature environments.

Example: specially formulated cement slurry

Composition of high-density cement slurries. Unit wt. %.

180º C

Material which replaces Portland cement, helping compaction

Density (kg/m³)	Cement	Wanter	Fluid Loss Reducer	Retarder	Dispersant	Mesh Slica Fume	Mn Weighting Agent	Slag	Resin
2.0	100	41	7	2.5	2	35	16	20	8
2.1	100	42	7	2.5	3	35	32	18	8
2.2	100	44	6	2.2	4	35	52	18	8
2.3	100	45	6	2	4.5	35	79	16	10

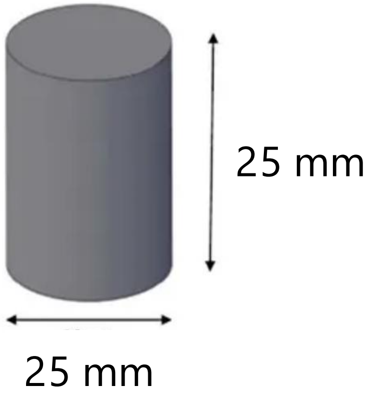
100 mesh: 150μ m ; 300 mesh: 48μm

Added material which in high temperatures, reacts with cement hydrated silicates to generate tobermorite and xonotlite, reducing the ratio of C/S from 2 to 3:1 to approximately 1:1

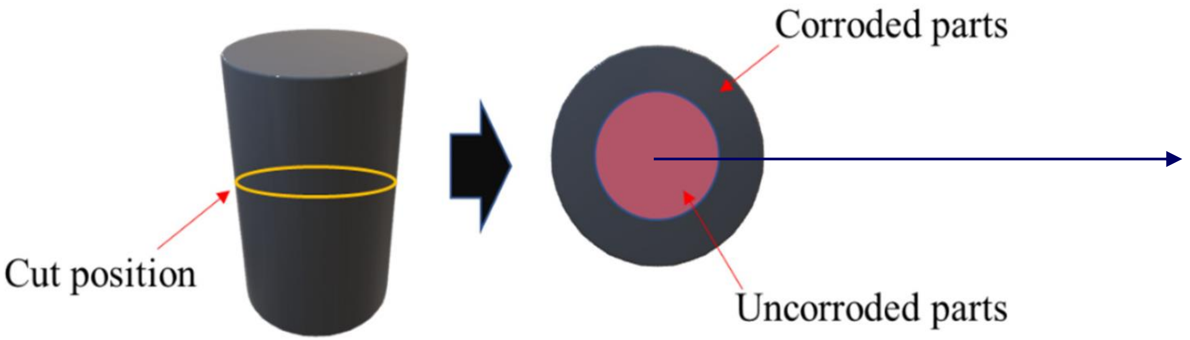
Material which protects cement matrix, mitigating corrosion

Example: specially formulated cement slurry

30 Mpa = 4.350 psi
180ºC



The cement cylinders were retrieved after 7 and 30 days for evaluation



Most integral part = alcaline region (presence of Ca), indicated by phenolphetalein coloration (red)

Example: specially formulated cement slurry

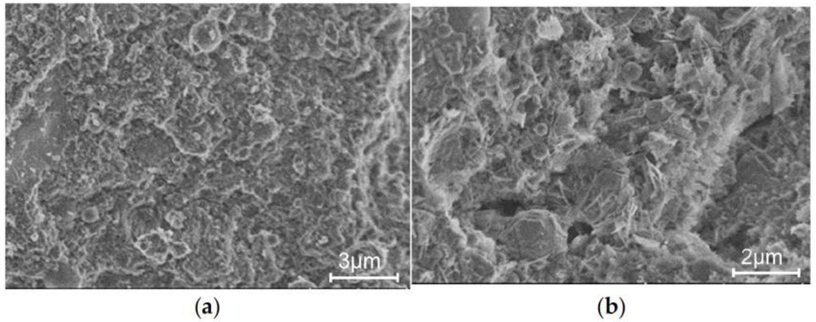


Figure 13. Morphology of 2.0 kg/m^3 cement sample: (**a**) non-corroded; (**b**) corroded.

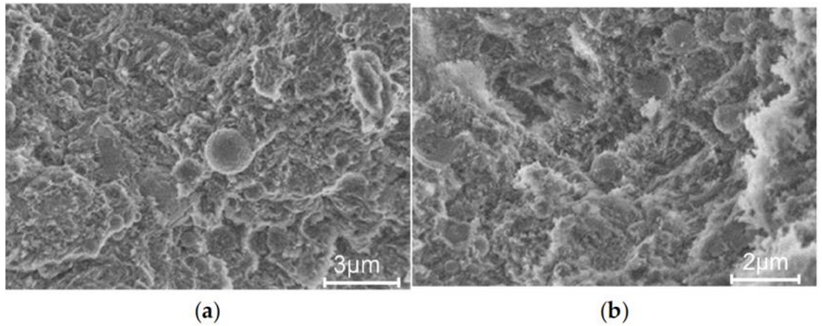
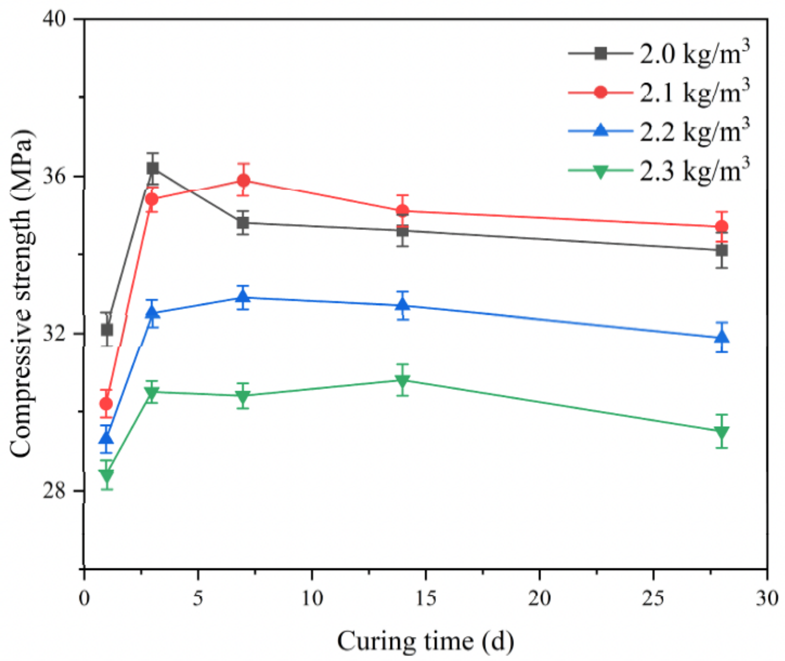
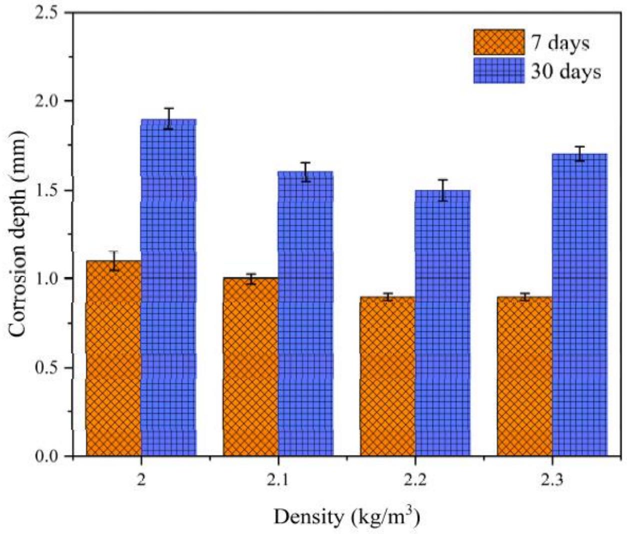
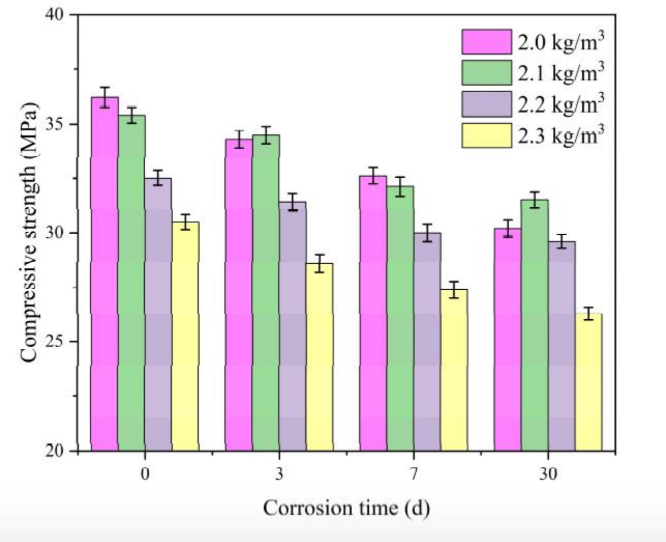


Figure 14. Morphology of 2.3 kg/m^3 cement sample: (**a**) non-corroded; (**b**) corroded.

Example: specially formulated cement slurry







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QUIZ TIME

Acid Attack

When does the acid attack produces a faster reaction:

1. Initial 7 days period
2. From 7 to 30 days (23 days period)

QUIZ TIME

Compressive strength

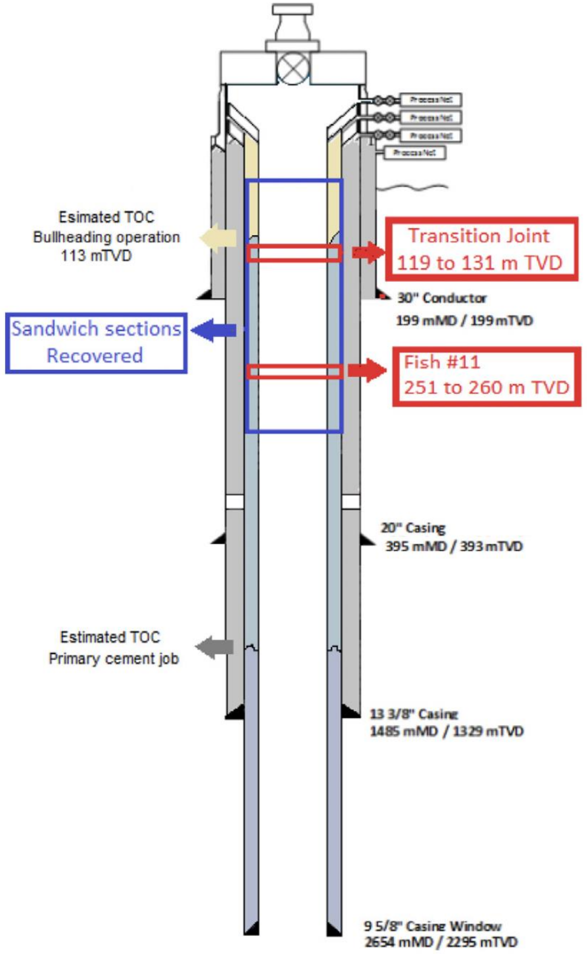
Which property is highly altered in this last slide?

1. Core density
2. Core permeability and porosity
3. Core strength

Conclusion

- CO_2 , H_2S and high temperatue environments represent serious challenges to the durability of set cement in oil/gas wells;
- Well intervention events such as steam or CO_2 injection, acid stimulation, hydraulic fracturing, well pressurization, or alike, may also negatively impact cement integrity
- Preventive strategies and perfiodical checks are essential to guarantee long term integrity of a well.

Investigation of well integrity of a 33 years old offshore well in Norway



69 m water depth

Well design showing the location of sections. In purple the twenty three recovered sections and in red the two sections, our object of study.

Investigation of well integrity of a 33 years old offshore well in Norway

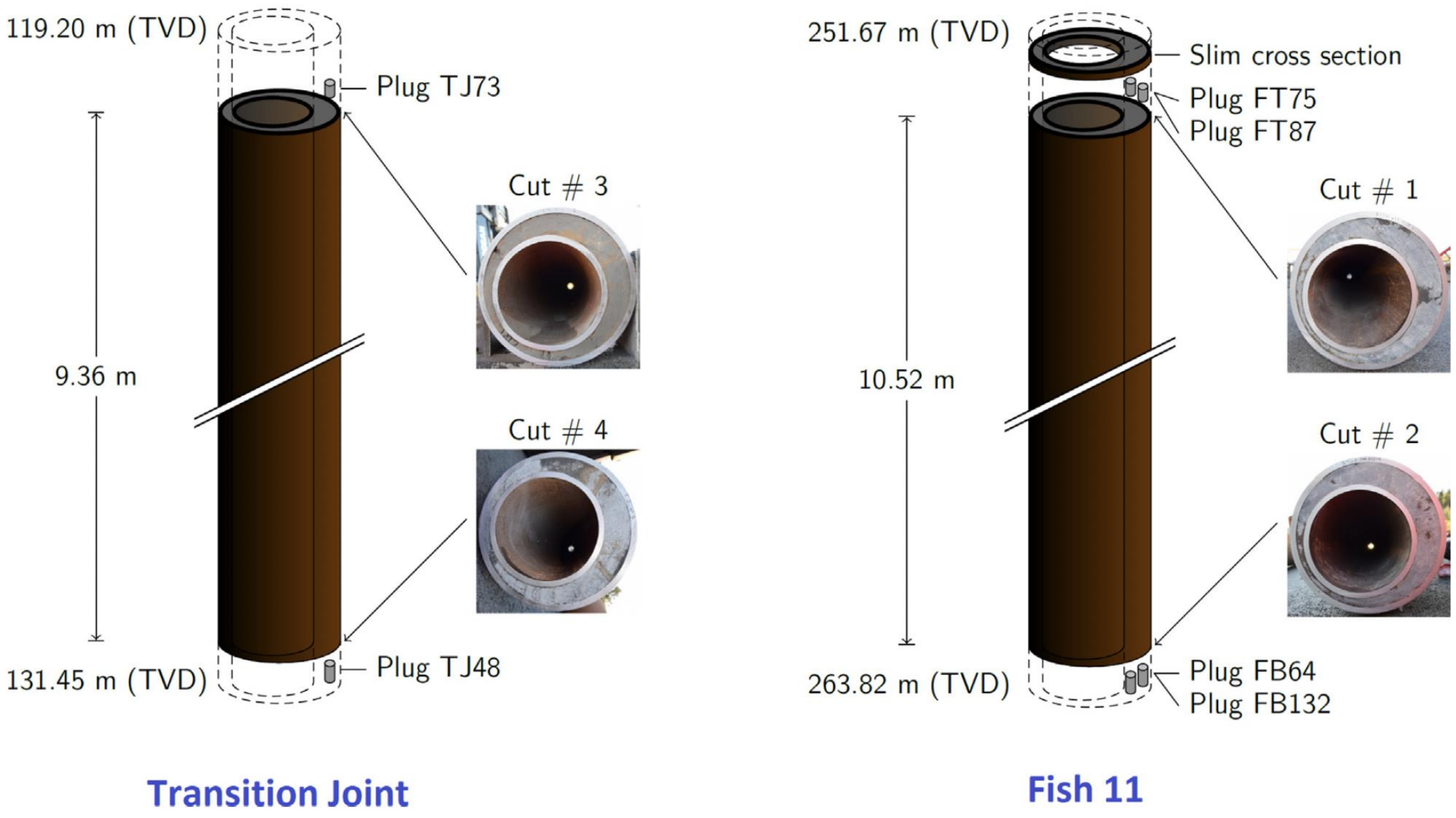


Fig. 2. Transition Joint and Fish # 11 diagram including pictures of the ends (Bottom and Top).

Investigation of well integrity of a 33 years old offshore well in Norway

Table 1 – Sandwich sections under study

	Transition Joint	Fish # 11
Well depth (m)	119.2-131-5	251.7-263.8
Final length (m)	9.36	10.56
Min. Sand off (m)	0.01057	0.01250
Max. Eccentricity %	70	64

Shallow depth (low temperature)

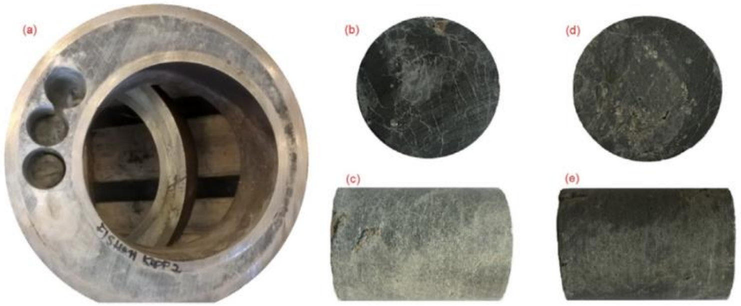


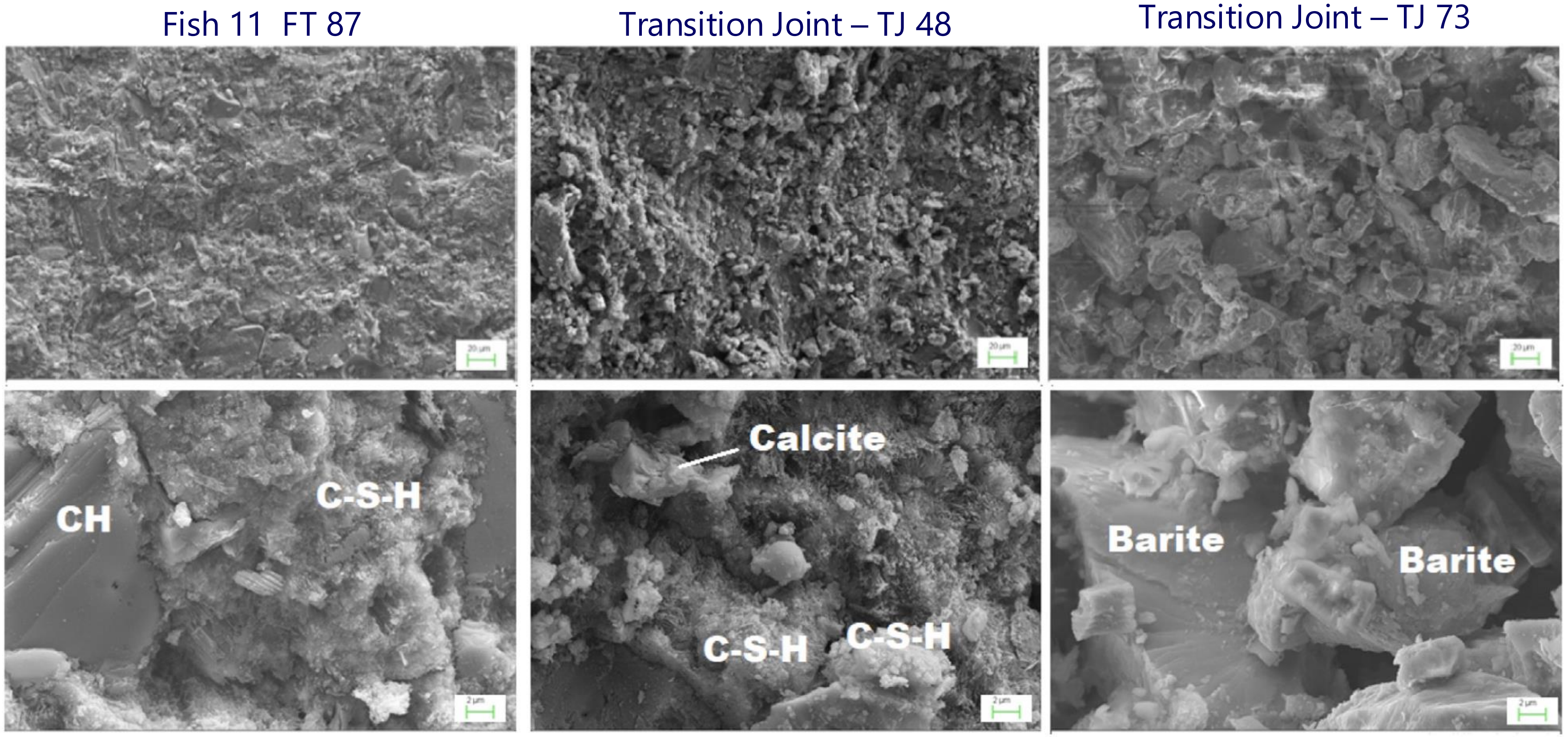
Fig. 3. Core plugs obtained from Fish 11 (Bottom). (a) Drilling of core plugs, (b) FB 64 top view, (c) FB 64 lateral view, (d) FB 132 top view and (e) FB 132 lateral view.

Investigation of well integrity of a 33 years old offshore well in Norway

Selection name	Core Plug	Petrophysical Properties			Mechanical Properties		Compositional Analysis		
		Porosity	Permeability	CT scan	E	UCS	SEM-EDS	XRF	XRD
Transition Joint	TJ48 TJ73	✓ ✓	✓ ✓	✓ ✓	✓	✓	✓ ✓	✓ ✓	✓
Fish# 11	FT 75 FT87 FB 64 FB132	✓ ✓ ✓ ✓	✓ ✓ ✓ ✓	✓ ✓ ✓ ✓	✓ ✓	✓ ✓	✓ ✓	✓ ✓ ✓	✓ ✓

CT: Computer Tomography Scanning | **E:** Young's Modulus | **UCS:** Uniaxial compressive strength | **SEM:** Scanning electron microscopy | **EDS:** Energy dispersive spectroscopy | **XRF:** X-ray Fluorescence | **XRD:** X-ray Diffraction.

Investigation of well integrity of a 33 years old offshore well in Norway



Comparison of SEM Images at magnifications 1.0 kX (upper panels) and 10.0 kX (lower panels) for material extracted from FT87, TJ47 and TJ 73 core plugs.

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