

# Chapter 4

## Types of Permanent Plugging Materials



Portland cement is the prime material used for zonal isolation and permanent P&A of wells. However, there are some concerns which persuade engineers to search for alternative materials to Portland cement. Therefore, this chapter will focus on different material types which might be used as permanent well barrier elements during permanent P&A, Table 4.1 [1, 2]. Some of these materials have already been used as permanent well barrier elements while some other have not. The criteria and requirements for the selection of material types for the permanent P&A varies for different authorities legislating P&A regulations.

### 4.1 Setting Materials

Throughout history, setting materials have played an important role and were used widely in the ancient world. The Romans found out that a setting material could be made which sets under water and it was used for the construction of marine structures such as harbors. Throughout time and with the development of science, different types of cementitious materials have been developed such as geopolymers, slag, and hardening ceramics [1]. The most known and studied type of cementitious materials is Portland cement.

#### 4.1.1 Portland Cement

In 1824, Joseph Aspdin took out a patent on a setting material he produced by calcining a mixture of limestone and clay at 2640 °F. The produced material looked like Portland stone, a widely-used building stone in England, and therefore he called his invention Portland cement. Since then, different types of Portland cement have been developed for different applications. When limestone (or other materials high in calcium carbonate) and clay or shale are calcined at 2640 °F, partial fusion occurs and clinkers are produced. A few percent of gypsum ( $\text{Ca}_2\text{SO}_4$ ) is added to the clinker and

**Table 4.1** Different material types which might be used as permanent well barrier element [1–4]

Type	Material	Examples
1	Cements (setting)	Portland cement, pozzolanic cements, blast furnace slag-based cement, phosphate cements, geopolymers, hardening ceramics
2	In situ formation	Shale, salt, claystone
3	Grouts (non-setting)	Unconsolidated sand or clay mixtures, bentonite pellets, barite plugs, calcium carbonate
4	Thermosetting polymers and composites	Resins, epoxy, polyester, vinylesters, including fiber reinforcements, urethane foams, phenol
5	Thermoplastic polymers and composites	Polyethylene, polypropylene, polyamide, Polytetrafluoroethylene (PTFE), Polyether Ether Ketone (PEEK), Polyphenylene Sulfide (PPS), Polyvinylidene Fluoride (PVDF), and polycarbonate, including fiber reinforcements
6	Metals	Steel, other alloys such as bismuth-based materials
7	Modified in situ materials	Barrier materials made from in situ casing and/or formation through thermal or chemical modification
8	Elastomeric polymers and composites	Natural rubber, neoprene, nitrile, Ethylene Propylene Diene Monomer (EPDM), Fluoroelastomer (FKM), Perfluoroelastomer (FFKM), silicone rubber, polyurethane, PUE and swelling rubbers, including fiber reinforcements
9	Gels	Polymer gels, polysaccharides, starches, silicate-based gels, clay-based gels, diesel/clay mixtures
10	Glass	

the blend is finely ground to make the cement. The gypsum controls the setting rate and can be replaced by other forms of calcium sulphate [5]. The major components of clinker are approximately 67% CaO, 22% SiO<sub>2</sub>, 5% Al<sub>2</sub>O<sub>3</sub>, 3% Fe<sub>2</sub>O<sub>3</sub>, and 3% of other components.<sup>1</sup> The clinker mainly contains four major phases: alite, belite, aluminate phase, and ferrite phase. The alite phase is tricalcium silicate (3CaO·SiO<sub>2</sub> or “C<sub>3</sub>S”) and constitutes 50–70% of normal Portland cement clinkers. The belite phase is dicalcium silicate (2CaO·SiO<sub>2</sub> or “C<sub>2</sub>S”) and constitutes 15–30% of normal Portland cement clinkers. The aluminate phase is a tricalcium aluminate (3CaO·Al<sub>2</sub>O<sub>3</sub> or “C<sub>3</sub>A”) and represents 5–10% of the most normal Portland cement clinkers. The ferrite phase is a tetracalcium aluminoferrite (4CaO·Al<sub>2</sub>O<sub>3</sub>Fe<sub>2</sub>O<sub>3</sub> or “C<sub>4</sub>AF”) and

<sup>1</sup>Clinker for construction cement.

represents 5–15% of normal Portland cement clinkers. Although there are several other phases such as alkali sulfates and calcium oxides, they represent minor amounts.

API categorizes the identified cements into nine different classes [6]:

- *API Class A*: This an ordinary Portland cement which is intended for use from surface to 6000 (ft) depth. It is not sulfate resistant and may be used when no special properties are required and well conditions allow.
- *API Class B*: It is ordinary Portland cement which is intended for use from surface to 6000 (ft) depth. It is available both as moderate and high sulfate-resistant.
- *API Class C*: It is called high early strength cement and used where early strength cement is required. It is intended for use from surface to 6000 (ft) and available as ordinary, moderate, and high sulfate-resistant types.
- *API Class D*: It is a retarded cement type which is intended for use from 6000 to 10000 (ft) depth and under conditions of moderate to high temperatures and pressures. It is available both as moderate and high sulfate-resistant types.
- *API Class E*: This is a retarded cement which is intended for use from 10000 to 14000 (ft) depth and conditions of extremely high temperatures and pressures. It is available both as moderate and high sulfate-resistant types.
- *API Class F*: It is intended for use from 10000 to 16000 (ft) depth and conditions of ultra-high pressures and temperatures. This class is available both as moderate and high sulfate-resistant types.
- *API Class G*: Intended for use as basic cement from surface to 8000 (ft) depth. It is manufactured in such a way that accelerators or retarders can be used to cover a wider range of well depths and temperatures. This class is available both as moderate and high sulfate-resistant types.
- *API Class H*: It is intended for basic cement use from surface to 8000 (ft) depth and can be used with retarders and accelerators to cover a wide range of well depths and temperatures. It is only available as moderate sulfate-resistant type.
- *API Class J*: It is known as special order only and intended for use from 12000 to 16000 (ft) depth. This class is for ultra-high pressure and temperature conditions and with accelerators or retarders wider ranges of well depths and temperatures can be covered.

Table 4.2 tabulates the properties of common oil well cements identified and classified by API. Cement class D, E, and F are seldom used for oil well cementing. The cement classes G and H are now the most common.

Table 4.3 presents typical physical properties of the various API classes of cement, given in Table 4.2, and cured at different pressures and temperatures.

There are some cementitious materials which have been or are used in oil well cementing effectively but they do not fall into any specific API category. These materials include [7]: (a) pozzolanic-Portland cements, (b) pozzolan-lime cements, (c) resins or plastic cements, (d) gypsum cements, (e) diesel oil cements, (f) expanding cements, (g) calcium aluminate cements, (h) latex cement, and (i) cement for permafrost environments.

*Pozzolanic-Portland cements*—This is a kind of blended cement which is produced by either intergrinding ordinary Portland cement clinker with gypsum and

**Table 4.2** API classification and properties of common oil well cements [7]

Type	Range of usage (ft)	Static temp. (°F)	Water ratio (gal/sk)	Slurry weight (lb/gal)	Volume (ft <sup>3</sup> /sk)	Remarks
Class A (Portland cement)	6000	60°–170°	5.2	15.6	1.18	No sulfate resistance. May be used well conditions allow
Class B (Portland cement)	6000	60°–170°	5.2	15.6	1.18	Moderate sulfate resistance
Class C (High early strength)	6000	60°–170°	6.3	14.8	1.32	Available in ordinary, moderate, and high sulfate-resistance types
Class G (Basic cement)	8000	200°	5.0	15.8	1.15	Compatible with accelerators or retarders for usage to cover the classes A through E
Class H (Basic cement)	8000 8000	200° 200°	4.3 5.2	16.4 15.6	1.06 1.18	Higher density, higher and lower water volume

pozzolanic materials or preparing each part separately and then blending them. Pozzolans are either natural or artificial reactive siliceous materials, processed or unprocessed, which start to hydrate in the presence of lime and water and develop cementitious properties. The source of most natural pozzolanic materials are volcanic ashes. The artificial pozzolans are produced by calcination of natural siliceous materials such as for example: clays, shales, rice husk ash, and certain siliceous rocks [8]. Fly ash is one of the artificial pozzolanic materials which is a combustion by-product of coal. In oilwell cementing, fly ash is added to cement to improve its strength and water-tightness.

*Pozzolan-lime cement*—Silica-lime or pozzolan-lime cements are blends of siliceous materials (e.g. fly ash), hydrated lime, and small quantities of a chemical activator (e.g. calcium chloride), which hydrate with water to produce calcium silicate. Their reaction rate is very slow at low temperatures compared to Portland cements. Therefore, these type of cements are recommended for wells where moderate to high temperatures are encountered. The use of these materials is not recommended in wells where temperature is less than 140 °F [9]. The reaction can be either accelerated or retarded by use of additives to cover a wide range of well conditions. Light weight, strength stability at high temperatures, low slurry cost, and less CO<sub>2</sub> emission are features of Pozzolan-lime cements.

**Table 4.3** Typical physical properties of the various API classes of cement [7]

Properties of API classes of cement							
		Class A	Class C	Classes G and H	Classes D and E		
Specific gravity (average)		3.14	3.14	3.15	3.16		
Surface area (range), cm <sup>2</sup> /g		1500–1900	2000–2800	1400–1700	1200–1600		
Weight per sack, lbm		94	94	94	94		
Bulk volume, ft <sup>3</sup> /sk		1	1	1	1		
Absolute volume, gal/sk		3.6	3.6	3.58	3.57		
Temperature (°F)	Pressure (psi)	Portland	High early strength	API Class G	API Class H	Retarded	
		<i>Typical compressive strength (psi) at 24 h</i>					
60	0	615	780	440	325	a	
80	0	1470	1870	1185	1065	a	
95	800	2085	2015	2540	2110	a	
110	1600	2925	2705	2915	2525	a	
140	3000	5050	3560	4200	3160	3045	
170	3000	5920	3710	4830	4485	4150	
200	3000	a	a	5110	4575	4775	
		<i>Typical compressive strength (psi) at 72 h</i>					
60	0	2870	2535	–	–	a	
80	0	4130	3935	–	–	a	
95	800	4670	4105	–	–	a	
110	1600	5840	4780	–	–	a	
140	3000	6550	4960	–	7125	4000	
170	3000	6210	4460	5685	7310	5425	
200	3000	a	a	7360	9900	5920	
Depth (ft)	Temperature (°F)						
	Static	Circulating	<i>High-Pressure thickening time (hours: minutes)</i>				
2000	110	91	4:00+	4:00+	3:00+	3:57	a
4000	140	103	3:26	3:10	2:30	3:20	4:00+
6000	170	113	2:25	2:06	2:10	1:57	4:00+
8000	200	125	1:40 <sup>a</sup>	1:37 <sup>a</sup>	1:44	1:40	4:00+

<sup>a</sup>Not generally recommended at this temperature

*Resins or plastic cements*—They are a mixture of either an API class A, B, G, or H cement with a mix of water liquid resins and a catalytic converter. These types of cements are used in small volumes for plugging open holes, and squeezing perforations. The recommended range of temperature is between 60 and 200 °F.

*Gypsum cements*—These types of cements are a mixture of API class A, G, or H cement with 8–10% of gypsum. The gypsum can be either in the hemihydrate

form ( $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ ) or the dihydrate form ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The gypsum cements set rapidly and they have high early strength with positive expansion properties. The expansion is in the range of 0.3%. Gypsum cements are used in lost circulation zones. The associated challenge with the use of gypsum cements is water solubility of the hardened cement and they can therefore only be used in wells where water does not exist. A solution for minimizing the water solubility of the hardened gypsum cements is to use equal volume of cement and gypsum [7].

*Diesel oil cements*—The diesel oil cements have been developed to selectively block off unwanted water production during drilling or in producing wells [10]. During the slurry design, an API cement class A, B, G, or H is mixed with diesel oil with a surface-active agent. These types of cements have unlimited pumping time as long as water does not meet the slurry. Water-in-oil emulsion cements are another type of diesel oil cement in which cement is mixed in a liquid phase consisting of oil as external or continuous phase and existing water as droplets. Low-fluid-loss characteristic, less damage to the oil-producing zones, and less damage to water-sensitive formations are some of the advantages of diesel oil cements and water-in-oil emulsion cements [11, 12].

*Expanding cements*—One of the drawbacks of Portland cement is its shrinkage which can create microannuli. Some degree of expansion can compensate the wellbore stress changes and improve the hydraulic and shear bond strengths [13]. Therefore, expansive cements or additive agents such as sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), pozzolans, anhydrous calcium sulfoaluminate ( $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$ ), calcium sulfate ( $\text{CaSO}_4$ ), and lime are introduced to the slurry. When sulfates and calcium aluminate components of cement are present, ettringite crystals, which are a hydrous calcium aluminum sulfate mineral are formed. As a result of the formation of the mineral crystals, pressure is developed and is the main expansion mechanism [14].

*Calcium aluminate cements*—These types of cements are known as high-alumina cements in which bauxite (aluminum ore) or other aluminous materials and limestone are heated in a furnace to be liquefied. Compared to Portland cement, these types of cements are low in silica content [5]. The calcium aluminate cements have high resistance to corrosive environments, rapid hardening properties, and are stable at high temperatures [15]. Addition of Portland cement to calcium aluminate cements results in flash setting.

*Latex cement*—Latex is commonly used to control gas migration, fluid loss and enhance the bonding properties of cements [16]. A latex cement is a blend of classes A, G, or H cement with latex either in liquid or powder form. The identified latexes are polyvinyl acetate, polyvinyl chloride, and butadiene styrene emulsions [7]. Butadiene styrene latexes are commonly used in oil well cementing; however, they are sensitive to temperature, mechanical energy, and free ions. As the latex has consisted of charged particles, latex demulsifies and precipitates in the presence of salts such as sodium chloride and calcium chloride [17]. One mitigation is the use of an anionic surfactant as an additive to the cement slurry to stabilize the latex cement in the presence of salts. Some investigators have shown the anti-corrosion ability of latex cements [18].

*Cement for permafrost environments*—Cementing conductor and surface casing in sub-freezing zones is a challenging task as Portland cement freezes, or never sets,

**Table 4.4** Compressive strength of gypsum cement for sub-freezing temperatures [21]

Pumping time (h)	Sodium Chloride, Percent <sup>a</sup>	Water Ratio (Ft <sup>3</sup> /sk)	Curing temperature, 20 °F				
			4 h	1 Day	3 Days	7 Days	14 Days
			(psi)				
2	10	048	470	855	615	600	1095
			Curing temperature, 15 °F				
				4 h	6 h	8 h	24 h
			(psi)				
2	10	048		345	530	635	545
3	10	048		38	ND	530	632
3	18	048		195	540	555	690

<sup>a</sup>By weight of mixing water  
 ND—Not determined

or permafrost melts as results of hydration heat [19]. There are some mitigations such as adding calcium chloride salt, short-chain alcohols such as methyl, propyl, or isopropyl to depress the freezing-point [20]. However, adding calcium chloride accelerates the hydration reaction and causes fast setting. Therefore, when calcium chloride is used to depress the freezing-point, retarders are used to postpone the setting time. There are four different types of blended cements available for permafrost environments; classes A and G API cements with calcium chloride, calcium aluminate cements with fly ash, refractory cements, and gypsum-cement blends [21]. Of these four, the gypsum-cement blends and refractory cements are mainly used in sub-freezing environments. Shryock and Cunningham [21] measured pumpability and compressive strength development of a gypsum-cement blend prepared for permafrost zones and found recipes that are applicable in permafrost areas, Table 4.4.

**4.1.1.1 Durability**

A plugging material is intended to withstand downhole conditions in an eternal perspective. Therefore, as eternal perspective is impossible, use of long-term durability knowledge of intended plugging materials is important. It is necessary to expose plugging materials to downhole chemicals, at downhole conditions, for different time intervals; sometimes up to a few years [22–25]. Then, the mechanical properties of plugging materials are characterized at different time intervals. Unfortunately, there is no international standard describing testing of plugging materials to qualify them for an eternal perspective. Thus, different researchers have selected different chemicals with different dosages to study the degradation of oilwell cements at downhole conditions. Vralstad et al. [25] aged neat class G cement, at downhole conditions, by exposing the samples to brine, crude oil, and H<sub>2</sub>S dissolved in brine for different

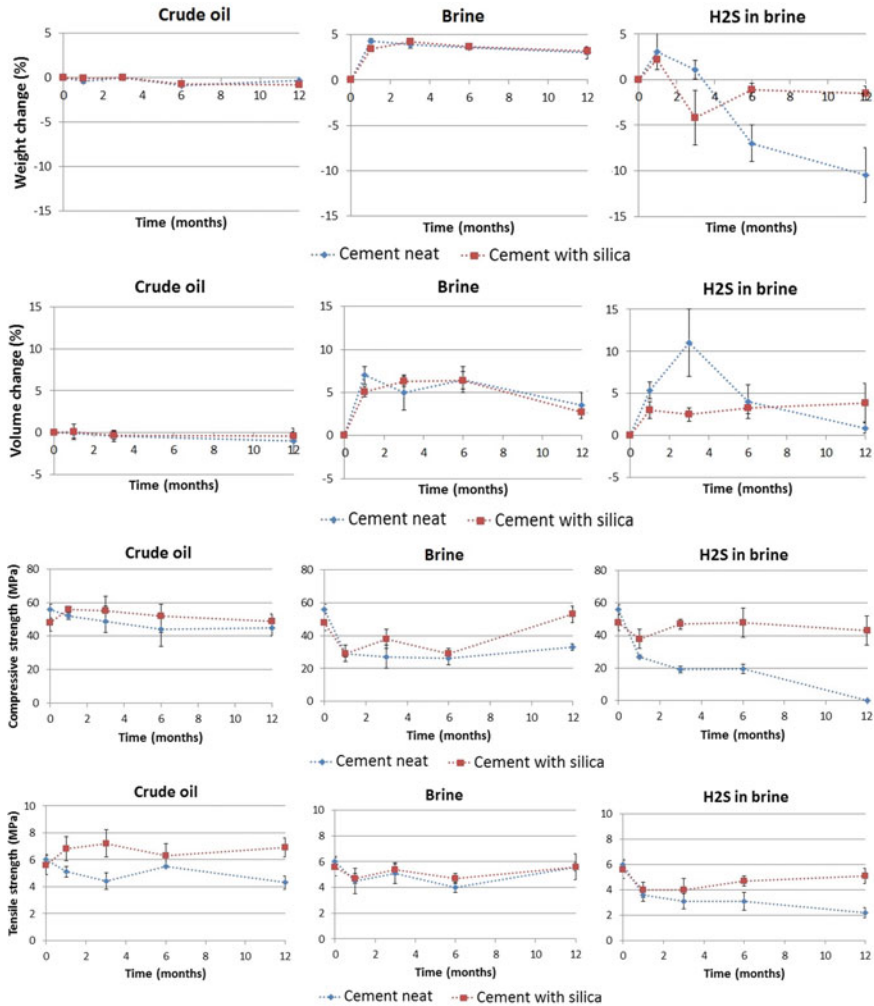


Fig. 4.1 Durability of neat class G cement exposed to downhole chemicals [25]

time intervals, up to 12 months. They also studied the weight and volume changes of the cement. Figure 4.1 shows the obtained results by Vrålstad et al. [25].

### 4.2 In Situ Formation (Formation as Barrier)

In some hydrocarbon fields, traditional sonic logs and ultrasonic azimuthal bond logs provide information of good bonding above the theoretical top of cement and at depths where there is no cement or where a poor cement job has been reported.



In addition, performed extended leak off (XLOT) tests show qualified seals [26]. The question is how this could be happened? In all of these cases, the used drilling fluids were known to have no setting properties. In addition, no casing collapses were reported. The only main remaining parameter is in situ formations which may have the potential to move toward or expand into the annular space and create a good seal, see Fig. 4.2. If the in situ formation moves and creates a good seal with sufficient strength, then it can be regarded as a most suitable permanent plugging material; as it has been standing in the overburden with intact long-term durability.

In order for the formation to move and create a good seal in the annular space, it should deform. *Deformation* is defined as changes in the shape or position of a rock body in response to stress. Stress is the internal resistance of rocks against the forces applied to deform the rock. Stress can be divided into two different stress types; *confining stress*, and *differential stress*. Whenever stresses acting on a rock are larger than its strength, rock can experience four different phenomena; folding, flowing, fracturing, or faulting. In a confining stress scenario, rock experiences a uniform stress in all direction. As a result of the acting confining stress, rock can expand or contract. Consider an in situ formation adjacent to an uncemented annulus which experiences equal stresses from overburden and the annulus fluid. The formation would not be able to move toward casing to seal the uncemented interval, see Fig. 4.3. So, confining stress is not the interest of this section and therefore, it is not discussed further. In differential stress scenarios, rocks experience unequal stresses in different directions. The resultant force acting on a rock may cause a *compressional stress*, *tensional stress*, or *shear stress*. Compressional stress is applied inward and triggers the rock to be squeezed, see Fig. 4.4a. Tensional stress is an outward stress which acts on a rock, the rock is pulled and subsequently it is elongated (see Fig. 4.4b). Shear stress is applied from one direction and cause movement of one part of the rock to pass the other which is still, (see Fig. 4.4c).

When the differential stresses act on a rock sample over time, deformation occurs. The deformation can be reversible or irreversible. *Reversible deformation* is a temporary shape change that is self-reversing after load is removed. In other words, the rock

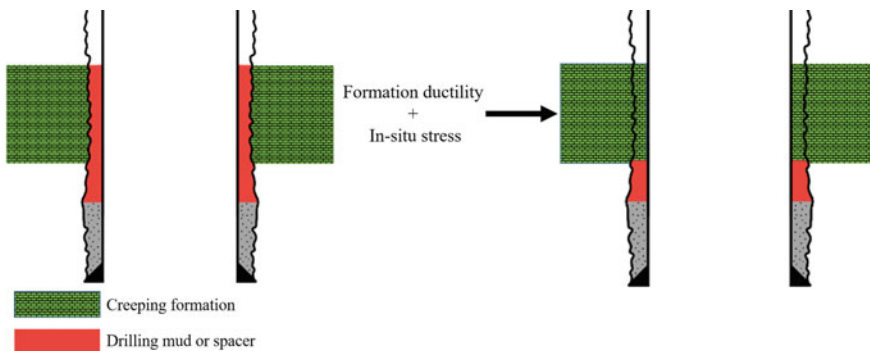
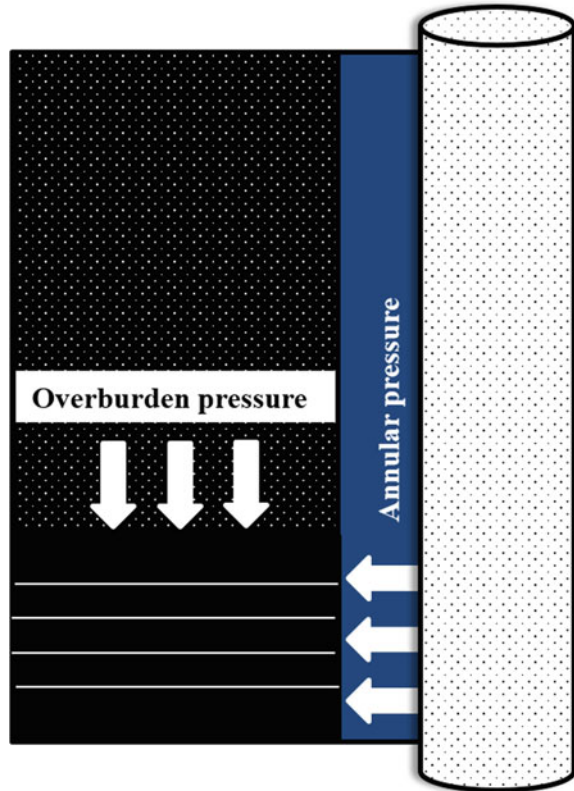


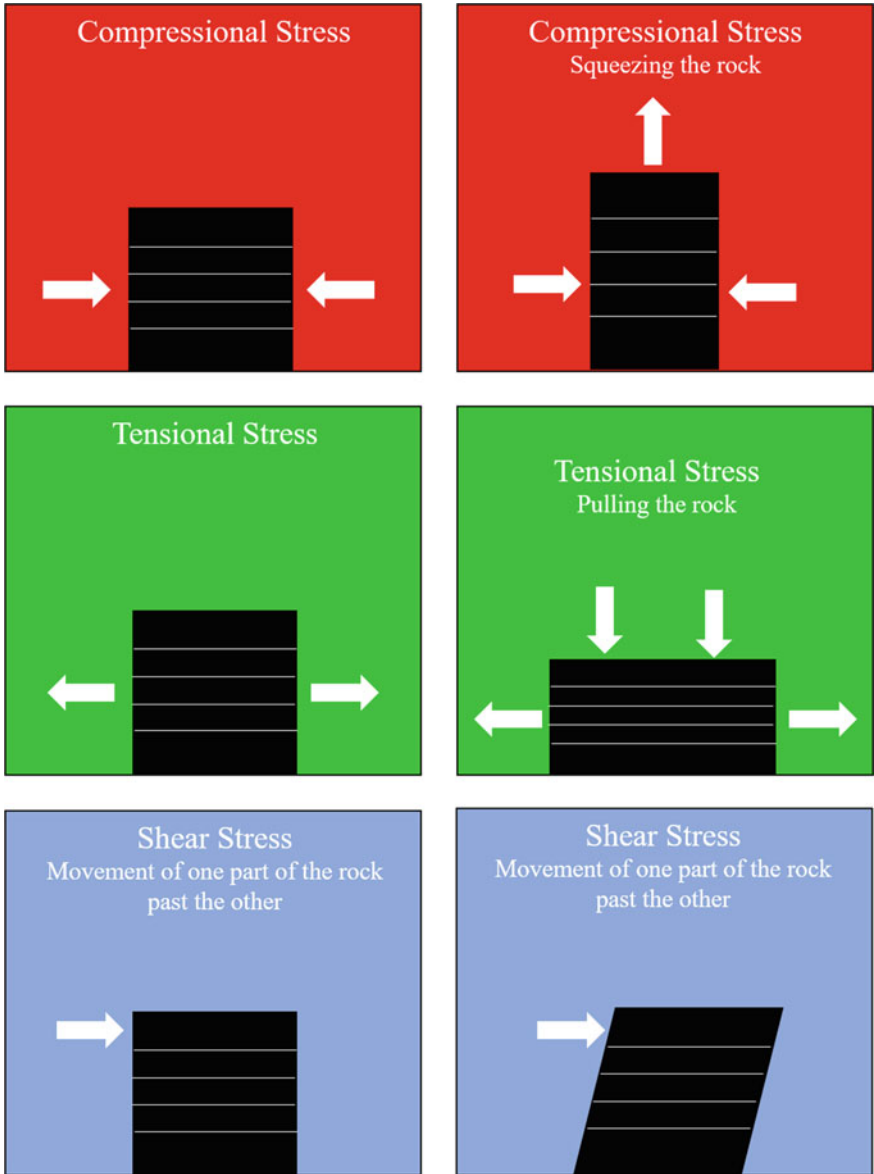
Fig. 4.2 In-situ formation moves toward the casing and create a seal

**Fig. 4.3** Equal stresses acting on a rock from all directions; overburden and annulus



returns to its original shape when the acting forces are removed. This type of deformation is known as *elastic deformation*. Elastic deformation happens at low levels of stress and it is recoverable after the stress is removed. In elastic deformation, the bonds between individual atoms and lattices are stretched, allowing the material to deform. Irreversible deformation is a permanent shape change that is not reversible when the load is removed. In other words, the rock does not return to its original shape when the acting forces are removed. The irreversible deformation is known as *plastic deformation*. In plastic deformation, the applied stress on a material cause microscopic dislocations such as edge and screw dislocations in the material lattices.

As we discussed earlier, when a differential stress is applied on a rock and the stress is higher than the rock strength, the rock deforms. The change in length of the rock, caused by stress, is called *strain*. In rock mechanics, a Stress-Strain diagram is plotted to measure the mechanical properties of rocks including elastic and plastic deformation limits. On a stress-strain diagram, when a stress is applied on a rock, strain behaves proportionally to the applied stress. The region where the stress-strain plot corresponds to an elastic deformation is linear, see Fig. 4.5. The slope is known as *modulus of elasticity*,  $E$ :



**Fig. 4.4** A rock sample which experiences unequal stresses from different directions; **a** compressional stress, **b** tensional stress, and **c** shear stress

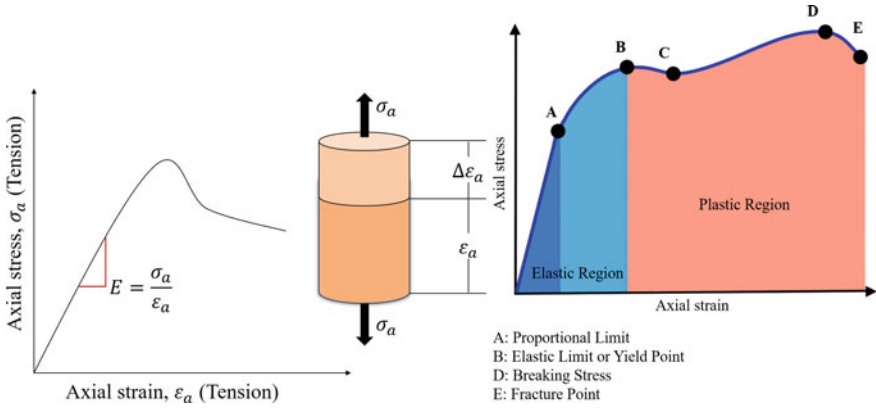


Fig. 4.5 A stress-strain diagram showing the elastic region (red) and plastic region (green)

$$Stress = E \times Strain \tag{4.1}$$

The stress where deformation shifts from elastic to plastic, is called the *yield stress*. The *yield strength* is the stress that is required to cause plastic deformation. In the plastic region, the stress-strain relationship is not linear and the material deforms much more rapidly compared to the elastic region, (see Fig. 4.5).

When a material experiences compressive stress or tensile stress, stress exists through the object, it can be elongated or shortened (see Fig. 4.6). The change in length of the material is estimated by Young’s modulus.

$$\Delta l = \frac{1}{E} \times \frac{F}{A} \times l_0 \tag{4.2}$$

where E is the Young’s modulus of the material, F is the applied force, A is the cross section where the force is applied, and  $l_0$  is the initial length of the material.

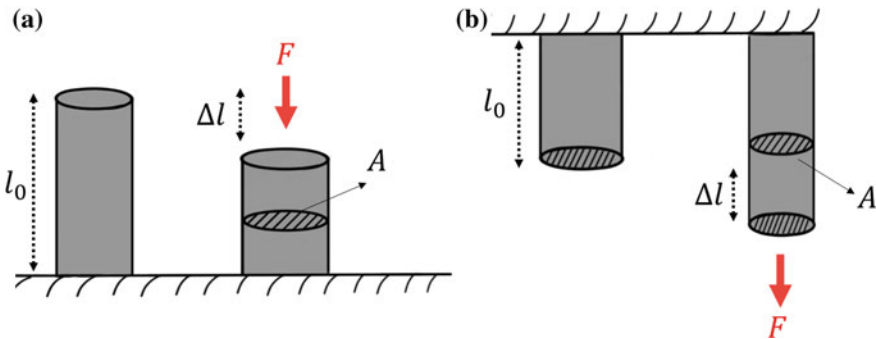


Fig. 4.6 Changes in length of a sample; a experiencing a compressive stress, b tensile stress

Shear modulus—When a material experiences a shear stress, its length can be shortened, Fig. 4.7. The length changes caused by a shear stress is characterized by its shear modulus, also known as modulus of rigidity:

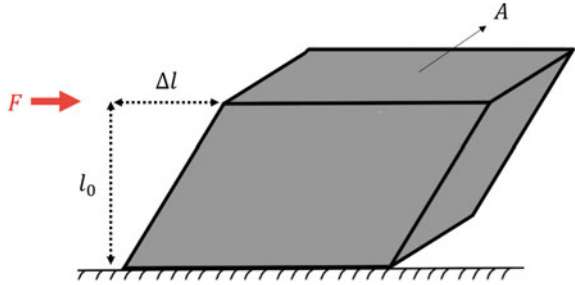
$$\Delta l = \frac{1}{G} \times \frac{F}{A} \times l_0 \tag{4.3}$$

where  $G$  is the shear modulus of material,  $F$  is the applied shear force,  $A$  is the surface area of material parallel to direction of the applied shear force, and  $l_0$  is the initial length of sample.

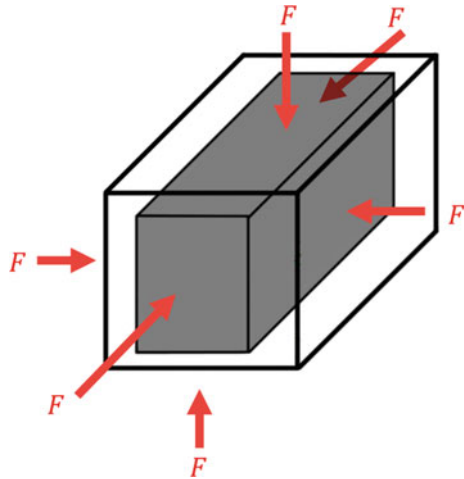
Bulk modulus—When a material experiences confining forces, from all directions, its volume can be reduced (Fig. 4.8). The volume change of the material is given by its bulk modulus:

$$\Delta V = -\frac{1}{B} \times \frac{F}{A} \times V_0 \tag{4.4}$$

**Fig. 4.7** Shear stress acting on a sample



**Fig. 4.8** Compressional forces acting on a material, equally, from all directions



where  $B$  is the bulk modulus of material,  $F$  is the confining pressure,  $A$  is the surface which force is applied on, and  $V_0$  is the initial volume of the material. The volume change can also be expressed in form of applied pressure or pressure change:

$$\Delta V = -\frac{\Delta P}{B} \times V_0 \quad (4.5)$$

Poisson's ratio—When a material experiences longitudinal stress from one direction, it will experience lateral strain. Therefore, the material will contract in one direction while elongating in a perpendicular direction, Fig. 4.9. The ratio of transverse contraction strain to longitudinal extension strain, in the direction of stretching force, is known as Poisson's ratio,  $\nu$ , given by:

$$\nu = -\frac{d\varepsilon_{tran}}{d\varepsilon_{axial}} \quad (4.6)$$

where  $d\varepsilon_{tran}$  is transverse strain (lateral strain), and  $d\varepsilon_{axial}$  is axial strain (longitudinal strain). Poisson's ration of materials is  $0 \leq \nu \leq 0.5$ .

Failure of a material can occur in elastic region or plastic region of the axial stress-axial strain curve. If the failure occurs in the elastic region, it is known as brittle failure and if it occurs in the plastic region, it is known as a ductile failure, Fig. 4.10.

In order to utilize in situ formations, which flow toward the annulus behind the casing, as a permanent well barrier element, the in situ formation should deform plastically and create a good seal. The plastic deformation which is time, stress and temperature dependent is known as *creep*. The creep, in rocks, is a slow deformation which can normally take long time. So it could be said that when in situ formation creeps toward the casing, it can create a seal and the seal can be used as a permanent plugging material.

If in situ formations experience a counter force from the annular pressure which is higher than the overburden stress, creep will not occur. Therefore, a formation barrier

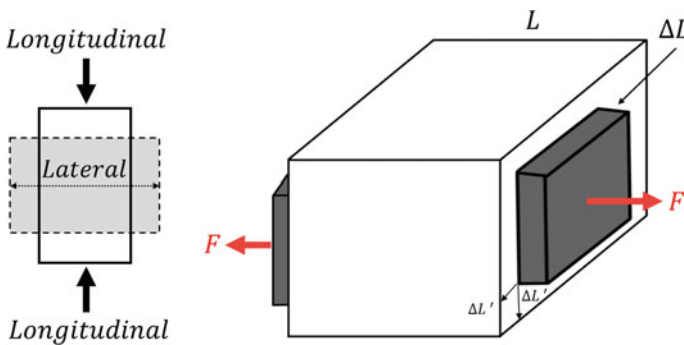


Fig. 4.9 Lateral strain and longitude strain acting on a sample

**Fig. 4.10** Brittle failure versus ductile failure

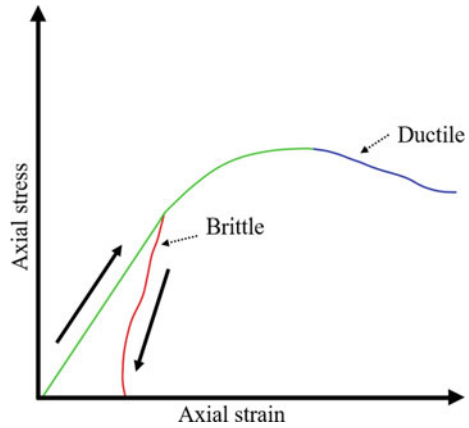
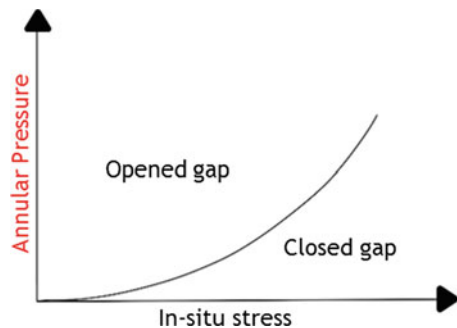


diagram is defined, Fig. 4.11. If the resultant stress of annular pressure and in situ stress falls in the “closed gap” region, a seal is created. However, if the resultant force falls in the “opened gap” region, then the annulus remains open and no seal is created.

It is important to differentiate between two phenomena; creep and swelling. Swelling is caused by the hydration of shales; heterogeneous porous media which has a matrix mainly of clays. Different theories have been presented as the driving mechanisms for swelling which include capillary pressure, hydraulic pore pressure imbalance, osmosis pressures, and the polar attraction of water molecule by the charged clay surfaces within the shale matrix [28–30]. According to the last theory, when water molecules move into a saturated shale body which is under constant contraction stress, the total volume of the body increases. Therefore, swelling strains develop at boundaries of clay layers. The swelling phenomenon is a reversible process upon dehydration. In other words, swelled shale is contracted as water molecules are drained. So, if swelling shale creates a seal in the annular space behind casing, it may not be a suitable material to be selected as a permanent plugging material.

**Fig. 4.11** Formation barrier map [27]

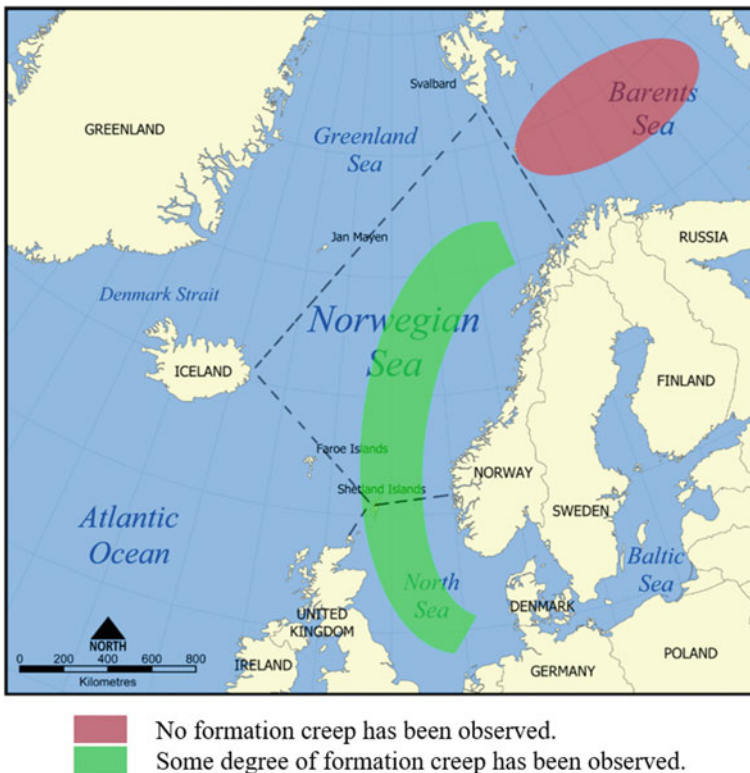


It is worthwhile to mention that not every formation creeps naturally but some do. As an example, in the Norwegian sector of the NCS a creeping formation has been reported in Staffjord A and Grane fields; some degrees of formation creep has been observed in all the fields North Sea and Norwegian Sea. However, no naturally creeping formation has been reported in the central/eastern Barents Sea, see Fig. 4.12.

Six different displacement mechanisms are suggested as driving mechanisms of formation movements [26, 31]:

- Shear or tensile failure,
- Compaction failure,
- Liquefaction,
- Thermal effect or expansion,
- Chemical effects,
- Creep.

*Shear or tensile failure*—Whenever exerted pressure by annular fluids is lower than the in situ overburden pressure, the formation falls into an unstable condition.



**Fig. 4.12** An overview of creeping formation and non-creeping formation on the Norwegian sector of the NCS [32]



If the differential pressure is high enough, then the formation experiences shear or tensile failure. Annular pressure drop is a common phenomenon in post-construction periods as the mud density of the annular fluid is reduced over time due to segregation of heavier components in the mud. Bond logs from some wells have shown that there are some lithological layers, between advancing formations, which have not moved. However, upper and lower formations behind have moved in the same well [26]. Thus, this driving mechanism alone is not the driver for formation movement.

*Compaction failure*—When a porous rock experiences a high hydrostatic pressure or pore pressure change, the grains may loosen or break. The movement of grains into the open spaces, which can be regarded as reorientation, results in a closer packing. This process is known as compaction failure [31]. Compaction failure is common in highly porous rocks such as sandstones. This mechanism is believed to be the subsequent response to movement and not the triggering process.

*Liquefaction*—Generally, any process that causes a non-liquid phase to behave in accordance with fluid dynamics is termed *liquefaction*. In rock mechanics, when a highly porous rock, which is loose (uncompacted), is fully or partially saturated and substantially loses its strength and starts to flow in response to any applied stresses, the process is called liquefaction. Recorded bond logs have shown good bonding which means that a solid material fills the annular space. Therefore, liquefaction is not the driving mechanism.

*Thermal effect or expansion*—Generally, increasing the temperature eases rock movement and causes some degree of expansion. However, during the production life of wells, the temperature change is small and besides, formation movement has been recorded in shallow depths where temperatures are not high. So, thermal effect cannot be the triggering mechanism.

*Chemical effects*—The movement of formation toward casing has been recognized in different wells which have been drilled with oil-based muds and water-based muds. So, the chemical effect cannot be the major contributor or be regarded as the main driving mechanism.

*Creep*—It is a time dependent parameter and happens over a long time. In some fields, the process of rock movement has been observed to be slow, however, in some wells it has been relatively quick. It can be concluded that creep can be regarded as the main mechanism in some fields while in others a combination of creep and shear failure can simultaneously be the driving mechanisms.

So far, in the North Sea, the lithology of identified creeping formations ranges in age from Oligocene (upper Tertiary) to Upper Jurassic. Another example of the use of creeping formation as well barriers is in the Gulf of Mexico where salt formations are used commonly as an exterior barrier [32].

As utilization of creeping formations is cost effective and a safe method, researchers have pursued an understanding of the mechanisms and conditions at which formations may start to creep. Studies show that the following parameters may activate or accelerate the formation creep: thermal treatment, chemical activation, changing annular fluid, and sudden pressure drop. Of these, sudden pressure drop has shown the potential to be a swift activation mechanism [27]. Changing the annular fluid may create a swelling effect and therefore, it might be of less interest.

**Table 4.5** Advantages and possible limitations for use of creeping formation as annular barrier

Advantages	Possible limitations
<ul style="list-style-type: none"> <li>• No section milling is required</li> <li>• Cost effective P&amp;A method</li> <li>• Reliable and durable plugging material</li> <li>• No HSE issue</li> <li>• Durable</li> </ul>	<ul style="list-style-type: none"> <li>• Not every formation creeps</li> <li>• Activation mechanisms of non-creeping formations are not well understood</li> <li>• Required length of plug defined by authorities</li> <li>• Qualification method is not clear</li> <li>• Artificially activation of formation may compromise its mechanical properties and long-term durability</li> </ul>

### 4.2.1 Durability

Formations have shown their long-term durability as cap rock. Therefore, no research work is performed to analyze the durability of creeping formations. However it is important to note that the artificial activation of a formation to creep may change its properties. Therefore, it is recommended to investigate the mechanical properties and the long-term integrity of activated formations. There are several advantages associated with utilization of formations as annular barriers, but also some limitations which are listed in Table 4.5.

## 4.3 Non-setting (Grouts)

Permanent plugging materials can be subjected to different stress scenarios during abandonment and post-abandonment such as tectonic stress, reservoir compaction, and temperature changes. Portland cement is the prime material used for permanent P&A. However, the associated concerns regarding Portland cement include but are not limited to brittleness, shrinkage, gas migration through the bulk material, long-term degradation by exposure to high temperatures and chemical substances, persuades researchers to seek for alternative materials. As solidified materials have some degree of brittleness, engineered unconsolidated materials have been suggested as an alternative plugging material [33]. These types of materials are also known with other names such as *grouts*, and *non-setting* materials [1]. Of these materials, unconsolidated sand or clay mixtures [33], bentonite pellets [34], calcium carbonate [35], and barite plugs [36] are the most well-known.

### 4.3.1 Unconsolidated Sand Slurries

Unconsolidated sand slurries consist of two phases; solid phase and liquid phase. The solid phase is sand with engineered Particle Size Distribution (PSD). The liquid

phase, known as the conducting fluid, is an inert fluid consisting of water, a small amount of dispersant and viscosifier which provides pumpability of the mixture. The mixture usually consists of approximately 75% solid and 25% of carrier fluid by volume [33], with a density of 17.9 (ppg). The slurry is a Bingham-plastic material which behaves as a rigid body at low stresses but flows at high stresses, Fig. 4.13.

The particles are kept packed by the electrostatic forces (Zeta potential<sup>2</sup>) between the solid particles and the conducting fluid [37]. Figure 4.14 shows a commercialized unconsolidated sand slurry which has been used for both temporary abandonment and permanent abandonment operations.

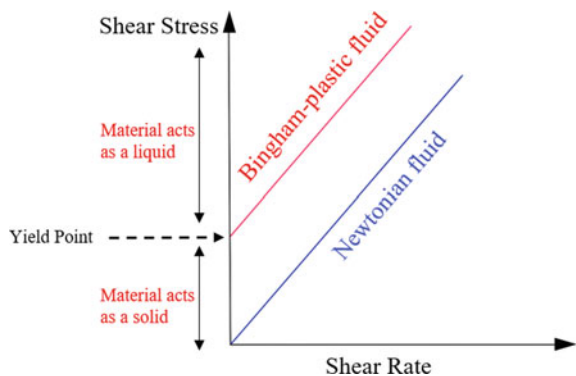
Figure 4.15 presents Scanning Electron Microscopy (SEM) image of a dehydrated unconsolidated sand slurry; different particle sizes are obviously visible.

An unconsolidated sand slurry does not set after placement and subsequently it does not shrink. As the material does not solidify, any introduced stress cannot fracture the material. When the downhole shear forces exceed the material limit, the material starts to flow and shear forces are reduced below the yield strength. This eventuates reshaping the material and the whole process is mechanical. As the unconsolidated sand slurry is made of quartz, it is thermodynamically stable and in the absence of carrier fluid, the plug remains homogenous. Table 4.6 presents advantages and possible limitations associated with unconsolidated sand slurries with regards to utilization for permanent P&A.

As the slurry does not set, the material could be used for zonal isolation and also during well construction provided a solid foundation exists. In addition, permeability of the plug cannot be measured directly, therefore, the Blake-Kozeny model is used [38]:

$$k = \frac{\epsilon^3}{(1 - \epsilon)^2} \frac{d_p^2}{150} \tag{4.7}$$

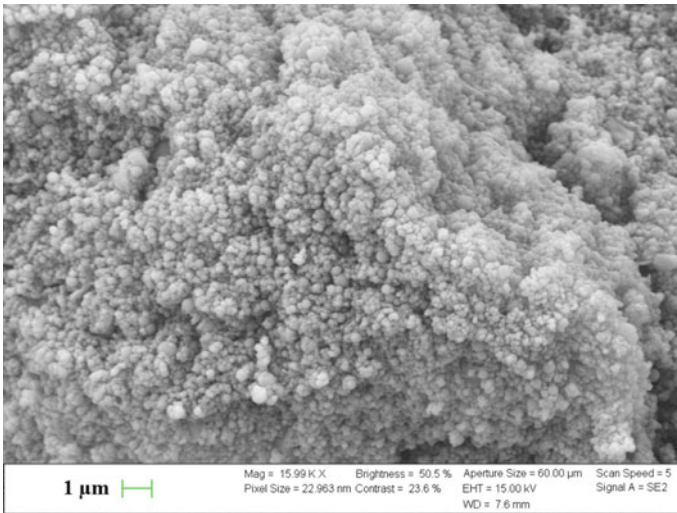
**Fig. 4.13** Flow behavior of a Bingham-plastic material



<sup>2</sup>The potential difference between the surface of solid particles immersed in a conducting liquid.



**Fig. 4.14** Unconsolidated sand slurry as an alternative plugging material. (Courtesy of FloPetrol Well Barrier)



**Fig. 4.15** SEM images of dehydrated unconsolidated sand slurry. (Courtesy of FloPetrol well barrier)

**Table 4.6** Advantages and possible limitations associated with unconsolidated materials with regards to permanent P&A

Advantages	Possible limitations
<ul style="list-style-type: none"> <li>• Flexible</li> <li>• Non-degradable</li> <li>• Non-shrinking</li> <li>• Non-toxic</li> <li>• Self-healing</li> <li>• Gas tight</li> <li>• No waiting on setting</li> </ul>	<ul style="list-style-type: none"> <li>• High Yield Stress may cause difficulties with regards to pumpability</li> <li>• It needs a permanent foundation to be used for permanent P&amp;A</li> <li>• No chemical bond strength to formation nor casing</li> <li>• No casing or formation seal if material is not confined</li> <li>• Conventional verification methods may not be applicable to find top of plug</li> <li>• Ineffective pumping may cause pack-off</li> </ul>

where  $d_p$  is the effective particle diameter,  $\epsilon$  is porosity of the medium, and 150 is an empirical factor which includes the geometrical terms. The Blake-Kozeny shows that the maximum permeability will be defined with micron-sized particles. By application of Darcy’s law and substituting the permeability term from Eq. (4.7), the flow velocity of an incompressible fluid through the medium is:

$$v = \frac{d_p^2}{150\mu} \frac{\epsilon^3}{(1 - \epsilon)^2} \frac{\Delta P}{\Delta L} \tag{4.8}$$

**Example 4.1** Consider an unconsolidated sand slurry with a porosity of 0.25 and an effective particle diameter of 1 and 0.1 micron. Estimate the permeability of the slurry.

**Solution** By using the Blake–Kozeny equation with a porosity of 0.25 and effective particle diameter of 1 micron, the permeability will be:

$$k = \frac{0.25^3}{(1 - 0.25)^2} \frac{1^2}{150} = 1.85 \times 10^{-4} \text{Darcy}$$

By selecting the effective particle diameter as 0.1 micron, the estimated permeability will be:

$$k = \frac{0.25^3}{(1 - 0.25)^2} \frac{0.1^2}{150} = 1.85 \times 10^{-6} \text{Darcy}$$

### 4.3.1.1 Pumpability

Placeability of any plugging material at downhole conditions is a primary requirement. Research activities have shown that the pumpability of unconsolidated sand slurries can be adjusted by adjusting the PSD design. The increase of conducting fluid volume should be considered carefully as inappropriate liquid content may increase

the distance between particles and consequently change the porosity and permeability. As unconsolidated sand slurries possess a very high yield stress, imposed pump friction may be challenging. Experiments have shown that the yield stress can be controlled by adjusting the PSD of sand slurries without increasing the volume of the conducting fluid [33, 39].

#### 4.3.1.2 Durability

As permanent plugging materials are intended to withstand downhole conditions with an eternal perspective, their long-term durability should be examined. The durability should normally be tested in accordance with recognized standards, however, there is no such standard for alternative materials to cement [37]. As unconsolidated sand slurries consist of quartz sand, silica fume, and crushed rocks, their interactions with downhole chemicals seems to be less probable.

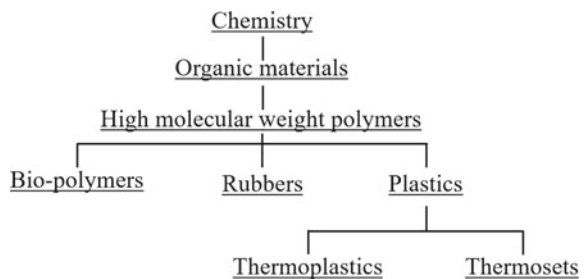
### 4.4 Thermosetting Polymers

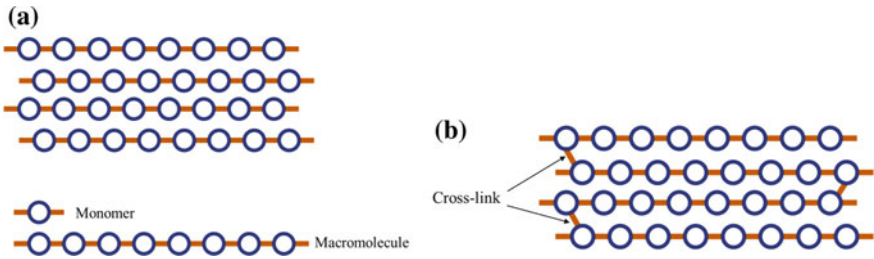
Thermosetting materials, also known as thermoset polymers, are organic compounds which are characterized by their three-dimensional structures and low molecular weight (<10000 g/mol). Figure 4.16 shows the chemical relationship between thermosetting polymers in chemistry. The term polymer is used to describe a macromolecule made of many monomers, repeating units, Fig. 4.17a. The rheological and mechanical properties of polymers depend on several factors including the monomer unit, the linkages between each monomer, intermolecular, and intramolecular forces which exists between polymers. Resins, synthetic polymers, are divided into two categories: thermosetting resins and thermoplastic resins.

Thermosetting polymers are cross-linked to one another, Fig. 4.17b, and due to the cross-links, these materials develop strength. The cross-links can break by heating or chemical interaction however, to break these bonds the conditions need to be severe.

Thermosetting resins set in the presence of catalysts, by application of heat and pressure or combination of these. The setting process is irreversible. It means that

**Fig. 4.16** Relationship of thermosetting materials in chemistry science [40]





**Fig. 4.17** Structure of polymers made of macromolecules and monomers

the resin cannot be reheated and remolded after setting. Thermoset plastic polymers are usually in liquid phase prior to curing, Fig. 4.18. The chemical reaction occurs during heating and results in the formation of strong covalent bonds, cross-links. Table 4.1 lists some examples of thermosetting plastic polymers. Thermoset plastic polymers usually undergo permanent or plastic deformation under load.

The stability of thermosetting materials depends on the density of cross-links and aromatic content of the polymer but generally speaking, there is a concern related to brittleness of the product with increase of cross-link density [40].

The history of thermosetting polymers for use in petroleum industry goes back to the 1960s when resins were suggested for remediating sand production [42]. Since then, they have been proposed and used for mud-loss control, remedial operations particularly for sealing tight channels, casing leaks, perforations and shoe and liner top squeezes, sand control, and production of resin-based cement [4, 41, 43–45]. As each wellbore is unique with respect to depth, downhole pressure and temperature, inclination, wellbore geometry, and formation strength, a range of additive materials are necessary to obtain the appropriate rheological and mechanical properties for

**Fig. 4.18** Physical and color appearance of a thermoset resin [41]. (Courtesy of WellCem AS)



thermosetting polymers. These materials include catalysts, accelerators, inhibitors, weight fillers, expansion agents and viscosifiers [46]. Catalyst or hardener is liquid which promotes the chemical reaction without itself being consumed. By increasing the concentration of catalysts, the rate of reaction of thermosets increases. The catalysts used for thermosetting polymers used in well cementing are usually acid-based. Accelerators are liquids which increase the rate of reaction at low temperatures. As elevated temperatures increase the rate of reaction, inhibitors or retarders are used to postpone the setting time of thermosetting polymers. The inhibitors are usually basic solutions. Thermosetting polymers have a wide range of densities so to modify their density, hollow spheres can be added to lower their density or heavy particles can be added to increase their density. As thermosetting polymers have relatively low, constant viscosity, addition of heavy particles may cause particle segregation. Therefore, viscosifiers are introduced to the resin mix to increase the viscosity and consequently the lifting capacity of the resin. Table 4.7 presents properties of thermosetting resins used for zonal isolation.

In order to wash the batch mixer, pumps, lines and all equipment, cleaners are used. Cleaners are chemical solutions, usually xylene or alcohol solutions, which cannot be disposed to sea or surroundings. Therefore, cleaners need to be handled and properly managed during and after use.

Table 4.8 presents a comparison between neat G Portland cement and a thermosetting resin developed for zonal isolation of hydrocarbon wells. However, shrinkage factor, shear bond strength, and hydraulic bond strength data for thermosetting resins are not publicly available.

**Table 4.7** Properties of a commercialized thermosetting synthetic polymer for cementing applications [46]

Property	Range
Density	6.2–20.8 ppg
Viscosity	10–2000 cp
Right angle set	Yes
Target temperature	68–300 °F
Pumpable through pipe	Yes
Miscible with water or well fluids	No
Decomposition temperature	900 °F
Setting time	Depends on curing temperature



**Table 4.8** Properties of hardened thermosetting resins designed for zonal isolation versus Neat G-cement [47]

	Compressive strength (kpsi)	Flexural strength (kpsi)	E-modulus (kpsi)	Failure flexural strain (%)	Permeability (mD)	
					Water	Oil
Thermosetting resin	11.2	6.5	325	1.9	$<0.5 \times 10^{-6}$	$<0.5 \times 10^{-6}$
Portland cement	8.4	1.4	537	0.32	$1.6 \times 10^{-3}$	<sup>a</sup>

<sup>a</sup>Not available

### 4.4.1 Main Degradation Mechanisms

Synthetic polymers degrade by different mechanisms depending on the structure and exposure conditions. Generally, organic polymers have five main degradation mechanisms: (a) physical, (b) chemical, (c) thermal, (d) hydrothermal, and (e) biodegradation [48, 49]. Physical degradation occurs as disruption of polymer morphology due to mechanical stresses, temperature, and time. It results in physical property changes which are reversible. Chemical degradation mainly occurs due to exposure to elevated temperatures, pollutants and micro- and macro-organisms. This type of degradation drastically changes the physical properties of organic polymers. This type of degradation is irreversible and occurs at the molecular level. Thermal degradation occurs above glass transition temperature and is irreversible. Hydrothermal degradation occurs at high temperatures in the presence of moisture and results in permanent physical property changes. In this condition, water molecules penetrate into the polymeric matrix and, at elevated temperatures, degenerates the interaction between polymer chains. One consequence could be swelling of the matrix and plasticization of the polymeric matrix. Biodegradation mechanism includes microorganisms to breakdown of thermosetting organic materials. With regards to utilization of thermosetting organic polymers, in petroleum industry, for zonal isolation and permanent P&A, a combination of these degradation mechanisms may be synergistic or antagonistic. Significant research is needed to understand the durability of thermosetting synthetic polymers at downhole conditions.

### 4.4.2 Long-Term Integrity of Thermosetting Resins

#### 4.4.2.1 Exposure to Downhole Chemicals

Long-term durability of any suggested plugging material needs to be investigated comprehensively as re-entry and repairing the barrier may be risky, time consuming

and even impossible. Interactions of thermosetting resins with downhole chemicals including brines, crude oil, H<sub>2</sub>S, CO<sub>2</sub>, and thermogenic gas at downhole conditions must be documented.

Preliminary experiments have been performed and published on durability of a commercially available thermosetting resin designed for oil well applications, Table 4.9. Crude oil, CO<sub>2</sub>, H<sub>2</sub>S, and methane gas were used as representatives of wellbore chemicals. Aging test results of thermosetting resin systems when exposed to brine are not available. However, hydrothermal degradation is one of the main degradation mechanisms.

Table 4.9 shows that crude oil degraded the thermosetting resin system at 212 and 266 °F but methane gas was inert and did not interact with the resin system. CO<sub>2</sub> did not affect the compressive strengths at both 212 and 266 °F but the flexural strength was affected at 266 °F. H<sub>2</sub>S reduced both the compressive and the flexural strengths at 212 and 266 °F.

There is a need to study weight and volume changes of thermosetting resin systems, during aging tests, when they are exposed to downhole chemicals.

#### 4.4.2.2 Thermal degradation

Usually in crystalline polymers, upon heat, the material transits from a hard and solid material to a liquid phase (see Fig. 4.19a). However, in amorphous polymers a reversible transition from a hard and relatively brittle state into a viscous and rubbery state occurs above specific temperatures (see Fig. 4.19b). This temperature is known as the glass transition temperatures ( $T_g$ ). Degradation kinetics of thermosetting resins above their glass transition temperature needs also to be evaluated.

For evaluation of thermal stability and degradation of thermosetting resins, two main parameters are studied: the activation energy ( $E_a$ ) and the pre-exponential constant ( $A$ ). The Arrhenius equation is used to quantify  $E_a$  and  $A$  above the glass transition temperature:

$$k = Ae^{-\frac{E_a}{RT}} \quad (4.9)$$

where  $k$  is the rate constant ( $s^{-1}$ ) for a particular reaction,  $T$  is the absolute temperature (Kelvins), and  $R$  is the universal gas constant. The natural logarithm of Eq. (4.9) yields:

$$\ln(k) = \ln(A) - \frac{E_a}{R} \frac{1}{T} \quad (4.10)$$

Equation (4.10) is the plot of a straight line with a slope of  $-\frac{E_a}{R}$  and an intercept at  $\ln(A)$ , see Fig. 4.19. So,  $k$  is the required parameter to find  $E_a$  and  $A$ . The thermal degradation of a resin system is modeled as a first order reaction as follows:

**Table 4.9** Exposure of thermosetting resin to different downhole chemicals [47]

Temperature (°F)	Property	Initial value	1-month	3-month	6-month	12-month
<i>Chemical: Crude oil 38° API (Curing pressure of 7250 psi)</i>						
212	Permeability (nD)	<0.5	ND	ND	ND	<4
212	Uniaxial compressive strength (psi)	11170 ± 725	7106 ± 1305	6091 ± 435	5800 ± 145	6526 ± 725
212	Flexural strength (psi)	6236 ± 435	4786 ± 725	3770 ± 145	3625 ± 145	3916 ± 145
266	Permeability (nD)	<0.5	ND	ND	ND	<20
266	Uniaxial compressive strength (psi)	11170 ± 725	5511 ± 145	5221 ± 435	4931 ± 145	5366 ± 145
266	Flexural strength (psi)	6236 ± 435	3625 ± 145	3625 ± 145	3190 ± 145	2900 ± 290
<i>Chemical: Methane 100% gas (Curing pressure of 7250 psi)</i>						
212	Permeability (nD)	<0.5	ND	ND	ND	<128
212	Uniaxial compressive strength (psi)	11170 ± 725	11458 ± 725	11312 ± 1015	11167 ± 725	13488 ± 580
212	Flexural strength (psi)	6236 ± 435	7687 ± 1015	6381 ± 2900	3335 ± 1595	7977 ± 1015
266	Permeability (nD)	<0.5	ND	ND	ND	Not possible <sup>1</sup>
266	Uniaxial compressive strength (psi)	11170 ± 725	11022 ± 1595	11748 ± 1885	12473 ± 1160	12183 ± 1305
266	Flexural strength (psi)	6236 ± 435	6816 ± 2900	8557 ± 3480	7832 ± 1450	8702 ± 435
<i>Chemical: CO<sub>2</sub>5% in N<sub>2</sub> gas (Curing pressure of 7250 psi)</i>						
212	Permeability (nD)	<0.5	ND	ND	ND	<79
212	Uniaxial compressive strength (psi)	11170 ± 725	10732 ± 870	11748 ± 1160	10587 ± 580	13343 ± 435
212	Flexural strength (psi)	6236 ± 435	4351 ± 1160	3770 ± 1450	3335 ± 1450	8122 ± 870
266	Permeability (nD)	<0.5	ND	ND	ND	Not possible <sup>1</sup>
266	Uniaxial compressive strength (psi)	11170 ± 725	7977 ± 435	Not possible <sup>a</sup>	10732 ± 435	11022 ± 435
266	Flexural strength (psi)	6236 ± 435	2755 ± 1160	Not possible <sup>1</sup>	5076 ± 145	5511 ± 290

(continued)

Table 4.9 (continued)

Temperature (°F)	Property	Initial value	1-month	3-month	6-month	12-month
<i>Chemical: H<sub>2</sub>S 5000 ppm (Curing pressure of 145 psi)</i>						
212	Permeability (nD)	<0.5	ND	ND	ND	Not possible <sup>a</sup>
212	Uniaxial compressive strength (psi)	11170 ± 725	5511 ± 145	7251 ± 290	7396 ± 290	7832 ± 435
212	Flexural strength (psi)	6236 ± 435	1885 ± 1015	2320 ± 290	2755 ± 1450	4496 ± 1160
266	Permeability (nD)	<0.5	ND	ND	ND	666
266	Uniaxial compressive strength (psi)	11170 ± 725	6961 ± 290	7832 ± 290	9282 ± 580	7251 ± 145
266	Flexural strength (psi)	6236 ± 435	2755 ± 1015	3190 ± 2755	2900 ± 1740	4206 ± 870

ND: Not determined

<sup>a</sup>Due to difficulties

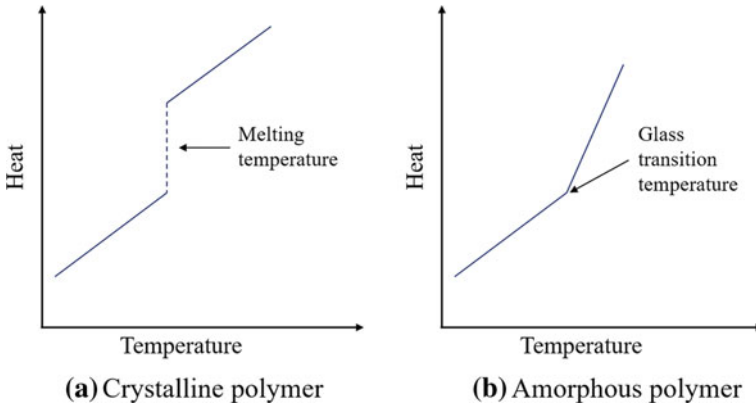


Fig. 4.19 Heat-Temperature plot for crystalline and amorphous polymers

$$-\frac{d[w]}{dt} = k[w] \tag{4.11}$$

where  $[w]$  is the relative weight to the initial weight of resin at time zero  $[w]_0$ ,  $t$  is the time. An integration of Eq. (4.11) yields:

$$\ln[w] = -kt + \ln[w]_0 \tag{4.12}$$

So, a plot of  $\ln[w]$  versus time yields the  $-k$ . Once the  $E_a$ , and  $A$  are known, the lifetime of a resin system at any temperature can be estimated. Research studies conducted on thermal characterization of different resin systems show that the lifetime of a resin system might be a concern for permanent P&A applications where downhole temperature is above the glass transition temperature ( $T_g$ ) [49]. If downhole temperature is above the glass transition temperature, the polymer has a higher free volume and higher permeability. Jones et al. [49] studied experimentally the thermal degradation of three resin systems at temperatures above their  $T_g$ . They estimated that for these systems, it will take between 60 and 150 years for the resins to lose 10% of their weight. However, the effect of high pressure on thermal degradation was not studied. They also concluded that above  $T_g$ , the resin degradation is intensified by increasing temperature. The  $T_g$  needs to be considered during the design of resin systems particularly for application in permanent P&A of wells. Advantages and possible limitations associated with the use of thermosetting resins for oil well cementing are listed in Table 4.10.

**Table 4.10** Advantages and possible limitations associated with thermosetting resins with regards to permanent P&A [47, 49, 50]

Advantages	Possible limitations and disadvantages
<ul style="list-style-type: none"> <li>• Gas tight (very low permeability)</li> <li>• Strong bond to formation and steel</li> <li>• Good mechanical properties</li> <li>• Chemically inert to wellbore fluids and rocks</li> <li>• Outdoor storage has no detrimental effects</li> <li>• No special equipment is required to prepare the mix</li> <li>• Low waiting on setting time</li> <li>• High tensile strength</li> <li>• The resins themselves are solid free (no grains)</li> </ul>	<ul style="list-style-type: none"> <li>• Usually brittle in solid state. Their brittleness is a function of polymer and curing pressure and temperature</li> <li>• Partly unknown long-term durability behavior</li> <li>• Interaction with brine and depolymerization</li> <li>• HSE issue regarding toxicity</li> <li>• Limited data available on pumpability</li> <li>• Unknown verification method when used for cementing casing</li> <li>• Possible interaction with workover fluid or mud</li> <li>• High-pH medium can deteriorate thermosetting polymers</li> <li>• Chemical shrinkage</li> <li>• No data available on hydraulic bond strength to formation and steel</li> </ul>

## 4.5 Metals

As discussed in Chap. 3, casing steel is not qualified as a permanent plugging material unless it is protected internally and externally by cement or another suitable material. There are some other types of metals with low melting point which have been suggested as permanent plugging materials including metal Bismuth, Gallium, Antimony, or low-melt-point eutectic alloys (Cerro alloys) [51, 52]. A eutectic alloy is a formulation of metal elements which melts and solidifies at a single temperature, which is lower than the melting points of the separate elements or of any combination. Eutectic alloys have no solidus or liquidus transition phases, completely solid or completely liquid. The most known eutectic alloy in the petroleum industry is bismuth based alloy. There are some concepts which suggest the use of eutectic alloys such as bismuth as a permanent barrier. Therefore, bismuth alloys are considered in detail in the following.

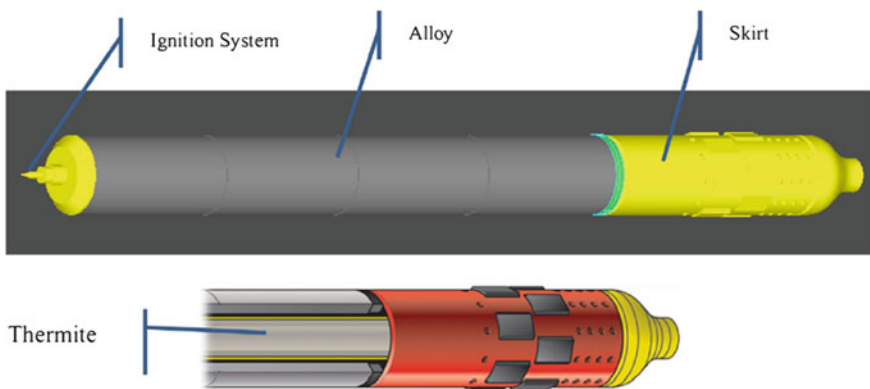
Bismuth is a metallic element with symbol Bi and atomic number of 83. Bismuth is brittle and a very weak radioactive material. Bismuth alloys have been laboratory tested and tested in a few field trials for use as a permanent plugging material, remediating sustained casing pressure, and shutting off water producing zones [52–54]. Bismuth based alloys are developed to create a metal to metal seal and their use in the petroleum industry goes back to the Schlumberger brothers in the 1930s. Bismuth based alloys are metals with very low melting point compared to other metals. A pure bismuth element has a melting point of 520 °F at ambient pressure and it expands upon solidification by 3%. However its alloys are reported to have much lower melting points, down to 174 °F, and with lower, albeit distinct, expansion factors.

As the metal alloys have very high densities, the liquid metal requires a foundation as a base. The expanding alloy is designed in a way that it has a melting temperature which is higher than the maximum anticipated well temperature. There have been two different techniques for placement of bismuth based alloys; the molten alloy is lowered to the desired depth within a container or the solid alloy is lowered to the desired depth and heated downhole. In the first technique, the molten alloy is carried with a container which can provide temperatures above the alloy melting point. When the alloy is at the desired depth, the container hatch is opened and the liquid alloy exits the container. The second technique is the most common and carried out in different ways including: heating once downhole using electric resistive or electromagnetic induction, in situ exothermic chemical reaction, or heated steam injection [51, 55].

One of the challenges concerning bismuth based alloys is the control of vertical heat propagation during installation of the plug when an in situ exothermic reaction is applied. A recent development employs a wireline operation as a bismuth alloy plug placement technique (see Fig. 4.20). The plug assembly consists of four main parts: ignition system, alloy jacket, inner tube and skirt. The inner tube, filled with thermite, passes through the bismuth alloy jacket. On ignition, the thermite reaction generates heat and once heated, the bismuth alloy jacket is melted. As the melted bismuth alloy has a high density and its positioning is not maintained, the skirt provides a mechanical support until the bismuth alloy plug cools down and solidifies. Using this method, the radial and vertical heat control is achieved more effectively.

Table 4.11 lists a wide selection of the expandable bismuth alloys with different ranges of melting temperatures.

There are advantages and some possible limitations associated with the utilization of alloy based plugging materials in permanent P&A operations, Table 4.12. As bismuth alloys create no physical bonding with casing, it relies on expansion to take mechanical and hydraulic loads. In addition, if the exerted force on the casing, due to expansion, is high then potential deformation of casing cement may occur which may put the integrity of the cement at risk.



**Fig. 4.20** The bismuth alloy plug placement assembly [55]

**Table 4.11** Some typical melting point temperature of bismuth based alloys [56–58]

Alloys	X: chemical formula	Range of melting point (°F)
Bi <sub>100-x</sub> Sn <sub>x</sub>	0–5	464–520
Bi <sub>100-x</sub> Cu <sub>x</sub>	0–45	520–1562
Bi <sub>100-x</sub> Hg <sub>x</sub>	0–45	530–520
Bi <sub>100-x</sub> Sn <sub>x</sub>	5–42	280–520
Bi <sub>100-x</sub> Pb <sub>x</sub>	0–44.5	255–622
Bi <sub>100-x</sub> Cd <sub>x</sub>	0–40	284–610

**Table 4.12** Advantages and possible limitations of bismuth based alloys for use in permanent P&A

Advantages	Possible limitations and disadvantages
<ul style="list-style-type: none"> <li>• Very low permeability or impermeable</li> <li>• Rigless operation</li> <li>• Non-explosive</li> <li>• No shrinkage</li> </ul>	<ul style="list-style-type: none"> <li>• No data available on sealing capability</li> <li>• No data available on durability</li> <li>• No chemical bonding to formation or casing</li> <li>• Uncertainty regarding downhole fluid displacement</li> <li>• Controlling vertical heat propagation during installation</li> <li>• No data available on hydraulic bond strength to formation and steel</li> <li>• Relatively brittle for a metal</li> <li>• Barrier verification method is not clear</li> <li>• Limited maximum length of barrier</li> <li>• Toxic if mercury or lead is used in the alloy</li> </ul>

## 4.6 Modified In Situ Materials

Recently a concept has been developed to do permanent P&A operations rigless and efficiently. In this concept, a target interval, in the wellbore, is selected and all the in situ elements are melted. Upon cooling, a solidified barrier is created from the in situ materials, Fig. 4.21.

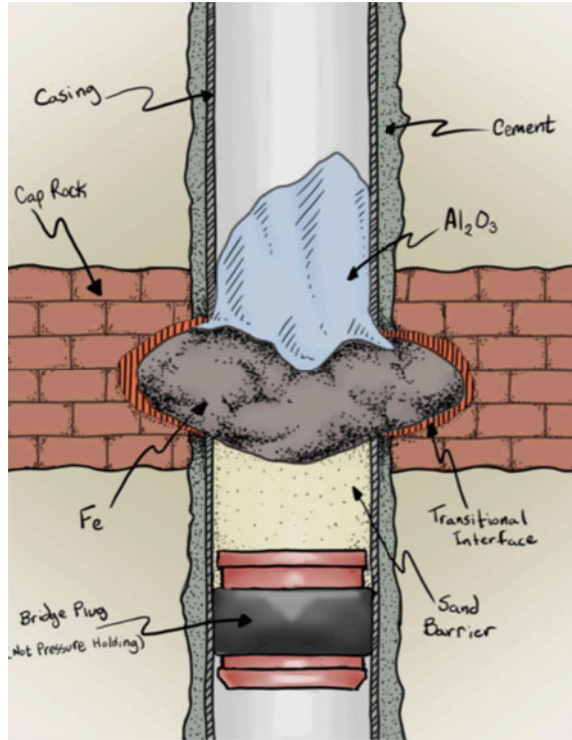
To melt the in situ materials, thermite is used as the source of energy to generate the required amount of heat. The term “thermit” was first introduced by Goldschmidt in 1903 [60]. *Thermite* is a metal powder which produces an effect by heat. The reaction is an exothermic reduction-oxidation reaction and it is ignited by heat. The reaction is written in a general form as [60]:



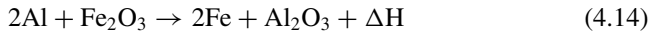
where M is a metal or an alloy, A is either a metal or a non-metal, MO and AO are their corresponding oxides, and  $\Delta H$  is the generated heat during the reaction.



**Fig. 4.21** Conceptual illustration of modified in situ materials as permanent barrier [59]



For example, the following is a well-known reaction:



The reaction is a single-replacement reaction in which aluminum reacts with iron oxide and takes the place of iron in the compound. Aluminium is more reactive compared to iron, it donates its electrons easier, and as a result of replacement, a large amount of energy is generated. The above-mentioned reaction creates temperatures in excess of 5432 °F. The reaction consumes small amounts of oxygen and it is self-sustained, Eq. (4.14). Generally speaking, a thermite reaction requires fuel metals and an oxidizer. The fuel metals include, but are not limited to, aluminium, titanium, magnesium, boron, zinc, and silicon. Of these, aluminium is of most interest as it has low cost and high boiling point. The oxidizers include, but are not limited to, bismuth (III) oxide, boron (III) oxide, silicon (IV) oxide, iron (II) oxide, and copper (II) oxide. Table 4.13 presents adiabatic temperatures for some thermite reactions,  $T_{ad}$ , and melting point of their products.

**Table 4.13** Adiabatic combustion temperatures and melting points of the product metals after Wang et al. [60]

Reaction	T <sub>ad</sub> (K) <sup>a</sup>	T <sub>mp</sub> of metal (K) <sup>b</sup>
I. Formation of common structural metals		
$\text{Al} + \frac{1}{2}\text{Fe}_2\text{O}_3 \rightarrow \text{Fe} + \frac{1}{2}\text{Al}_2\text{O}_3$	3622	1809
$\text{Al} + \frac{3}{2}\text{NiO} \rightarrow \frac{3}{2}\text{Ni} + \frac{1}{2}\text{Al}_2\text{O}_3$	3524	1726
$\text{Al} + \frac{3}{4}\text{TiO}_2 \rightarrow \frac{3}{4}\text{Ti} + \frac{1}{2}\text{Al}_2\text{O}_3$	1799	1943
$\text{Al} + \frac{3}{8}\text{Co}_3\text{O}_4 \rightarrow \frac{9}{8}\text{Co} + \frac{1}{2}\text{Al}_2\text{O}_3$	4181	1495
II. Formation of refractory metals		
$\text{Al} + \frac{1}{2}\text{Cr}_2\text{O}_3 \rightarrow \text{Cr} + \frac{1}{2}\text{Al}_2\text{O}_3$	2381	2130
$\text{Al} + \frac{3}{10}\text{V}_2\text{O}_5 \rightarrow \frac{6}{10}\text{V} + \frac{1}{2}\text{Al}_2\text{O}_3$	3785	2175
$\text{Al} + \frac{3}{10}\text{Ta}_2\text{O}_5 \rightarrow \frac{6}{10}\text{Ta} + \frac{1}{2}\text{Al}_2\text{O}_3$	2470	3287
$\text{Al} + \frac{1}{2}\text{MoO}_3 \rightarrow \frac{1}{2}\text{Mo} + \frac{1}{2}\text{Al}_2\text{O}_3$	4281	2890
$\text{Al} + \frac{1}{2}\text{WO}_3 \rightarrow \frac{1}{2}\text{W} + \frac{1}{2}\text{Al}_2\text{O}_3$	4280	3680
$\text{Al} + \frac{3}{10}\text{Nb}_2\text{O}_5 \rightarrow \frac{6}{10}\text{Nb} + \frac{1}{2}\text{Al}_2\text{O}_3$	2756	2740
III. Formation of other metals and non-metals		
$\text{Al} + \frac{1}{2}\text{B}_2\text{O}_3 \rightarrow \text{B} + \frac{1}{2}\text{Al}_2\text{O}_3$	2315	2360
$\text{Al} + \frac{3}{4}\text{PbO}_2 \rightarrow \frac{3}{4}\text{Pb} + \frac{1}{2}\text{Al}_2\text{O}_3$	>4000	600
$\text{Al} + \frac{3}{4}\text{MnO}_2 \rightarrow \frac{3}{4}\text{Mn} + \frac{1}{2}\text{Al}_2\text{O}_3$	4178	1517
$\text{Al} + \frac{3}{4}\text{SiO}_2 \rightarrow \frac{3}{4}\text{Si} + \frac{1}{2}\text{Al}_2\text{O}_3$	1760	1685
IV. Formation of nuclear metals		
$\text{Al} + \frac{3}{16}\text{U}_3\text{O}_8 \rightarrow \frac{9}{16}\text{U} + \frac{1}{2}\text{Al}_2\text{O}_3$	2135	1405
$\text{Al} + \frac{3}{4}\text{PuO}_2 \rightarrow \frac{3}{4}\text{Pu} + \frac{1}{2}\text{Al}_2\text{O}_3$	796	913

<sup>a</sup>Adiabatic temperature<sup>b</sup>Melting point temperature

Different combinations of the fuel metals and oxidizers generate different energy levels in a controlled manner. This method is known as “*dilution*” to control the amount of generated heat. When sufficient energy is produced, downhole equipment such as casing, cement, control lines and a portion of the in situ formation is melted. However, achieving high enough energy to melt the downhole equipment requires a certain amount of thermite, depending on the type of fuel and oxidizer.

The product of the reaction is usually a heavier metallic phase and a lighter oxide phase. Due to gravity, the lighter phase migrates upward and the heavier phase moves downward. For oil well applications, the freezing point is critical whereas solidification of the product prior to migration of the lighter oxide phase may result in a discontinuous barrier.

### 4.6.1 Barrier Establishment

A mechanical plug is required to be installed as a foundation for the molten materials prior to cooling. Because the high temperature may damage a mechanical plug, sand is placed on top of it. The wireline tool is equipped with a jacket which contains thermite and an igniter. This method employs a wireline operation to establish the barrier. The tool consists of four main parts: heavy load, separator, thermite pool, and igniter, (see Fig. 4.22a). The wireline provides the electrical power required to ignite the thermite mixture. When the thermite reaction is initiated, the thermite available in the thermite pool gets consumed in the reaction, and the reaction heats and melts the adjacent equipment. As the generated energy is high, rapid expansion of downhole fluids, at shallow depths, may be a concern. Therefore, a heavy load is applied to the thermite pool to compress the barrier while cooling (see Fig. 4.22b). As the high energy may melt the heavy load, a separator protects it. When the barrier is established, the heavy load and separator are retrieved (see Fig. 4.22c).

Controlled heat propagation, both in radial and vertical direction, is one of the challenges associated with this method. When a barrier is established, the transition area between the modified and non-modified materials needs to be qualified. Currently, there is no established methodology. In addition, limited data availability is another potential limitation besides, concerns associated with durability of the barrier, Table 4.14.

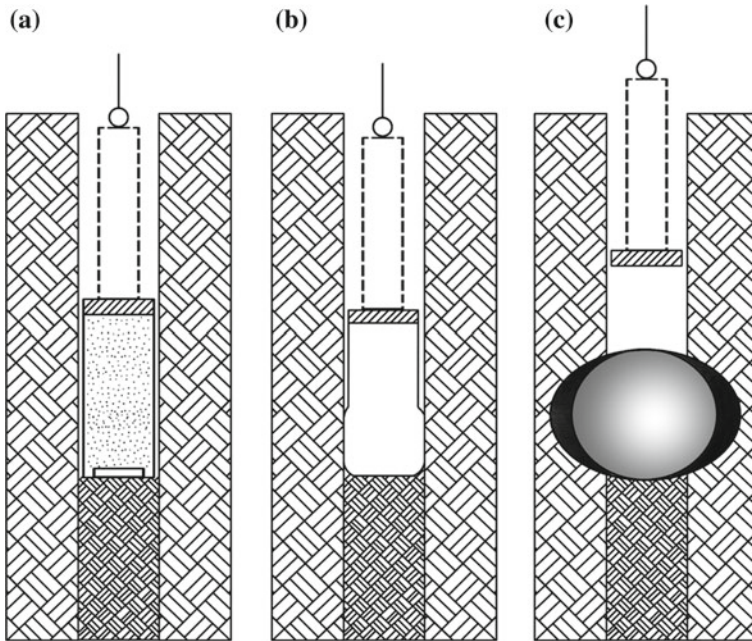


Fig. 4.22 Permanent barrier establishment by modified in situ materials method

**Table 4.14** Advantages and possible limitations concerned with modified in situ materials [59–62]

Advantages	Possible limitations and disadvantages
<ul style="list-style-type: none"> <li>• Rigless based concept</li> <li>• Safe to handle and low equipment intensity</li> </ul>	<ul style="list-style-type: none"> <li>• Barrier mainly consists of iron which associates to a long term durability concern</li> <li>• Presence of downhole fluids may compromise the sealability of barrier while establishing barrier</li> <li>• Maximum length of established barrier</li> <li>• Minimum hole diameter to run the tool in</li> <li>• Gravity force, in deviated sections, can cause segregation of the plug when it is in liquid phase</li> <li>• Contraction upon cooling and solidification may introduce micro cracks</li> <li>• Limited data availability</li> <li>• Not commercialized</li> </ul>

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