Chapter 3 Specification for Permanent Plugging Materials



Portland cement is currently the prime barrier material used in the petroleum industry for zonal isolation and permanent well abandonment. In addition, the industry considers alternative plugging materials. Therefore, it is necessary to consider functional requirements, operating conditions and qualification procedures for any newly developed alternative plugging material.

3.1 Material Requirements for Permanent Barriers

In order to qualify the well barrier for its intended use, some requirements are necessary to be defined. These requirements are called *Well Barrier Acceptance Criteria* (WBAC) and include functional, and verification requirements of the well barrier [1]. The main functional characteristics of permanent barrier materials are addressed as [1, 2].

- 1. Very low permeability or impermeable,
- 2. Long-term durability at downhole conditions,
- 3. Non-shrinking,
- 4. Ductile or non-brittle,
- 5. Resistance to downhole fluids and gases, and
- 6. Sufficient bonding to casing and formation.

3.2 Functional Requirements of Permanent Well Barrier Elements

A permanent well barrier element has to fulfill a number of functional requirements including sealing capability, bonding properties, downhole placeability, durability, and reparability. These requirements are discussed in this chapter in more detail.

3.2.1 Sealing Capability

The main function of a permanent barrier is to seal a potential and prevent the movement of fluids. The sealability of a material is a function of its permeability and bond strength. However, definition of impermeability is a controversial subject as most, if not all, materials have some degree of permeability for some elements. For example, cap rocks have some permeability within the range of $10^{-3}-10^{-6}$ millidarcy. It means that in the context of permanent well barrier materials, it is inevitable that a fluid within the well will ultimately migrate through a barrier, even though at a low rate. Table 3.1 presents permeability of some materials.

In order for a leak to occur, fluids must be able to enter into a barrier and breakthrough must happen. Then the definition and investigation of permeability gets its meaning. A fundamental requirement for an effective seal is that the *entry pressure* of the sealing material shall be higher than the capillary forces of fluids in the formation beneath. The *seal entry pressure*, the seal capacity, is the capillary pressure at which fluid pressure exceeds the capillary entry threshold and therefore, fluid leaks into the pore space of the barrier material. This is dependent on both barrier and fluid parameters. Barrier parameters include the size distribution of connected pore throats. Fluid parameters include the present fluids (e.g. water, oil or gas), fluid density, and *Interfacial Tension* (IFT) of the fluids.

The capillary entry pressure $(dynes/cm^2)$ is defined by Eq. (3.1) [5].

$$P_c = \frac{2\sigma(\cos\theta)}{r} \tag{3.1}$$

where σ is the interfacial tension (dynes/cm), θ is the contact angle of the water with the pore surface (degrees), and r is the pore radius (microns). Capillary entry pressure, also known as seal capacity, could potentially be defined as a means of resisting permeation of WBE by fluids. Among the contributing factors in capillary entry pressure, the contact angle and pore radii are prone to modification with time. In the case of water as the entering fluid, the capillary entry pressure is only exceeded when the contact angle between WBE and water is greater than 90°.

Material	Permeability (millidarcy)
Portland cement (neat class G) [4] ^a	10 ⁻²
Shale	$10^{-3} - 10^{-5}$
Granite	$10^{-3} - 10^{-4}$
Halite	$10^{-7} - 10^{-9}$
Anhydrites	$10^{-5} - 10^{-7}$

Table 3.1 Permeability of some materials [3]

^aAlthough neat class G Portland cement has such a permeability, use of cement permeability reduction additives reduce the permeability significantly

3.2.1.1 Methods for Measuring Capillary Pressure

Due to the complex structure of pores, it is impossible to use Eq. (3.1) to calculate the capillary pressure of porous media. Therefore, laboratory measurements have been developed and are the most reliable methods for capillary pressure measurements. Methods for measuring capillary pressure are categorized as:

- · Mercury methods
- Porous-plate method, and
- Centrifuge method.

Mercury method—For experimental convenience, it is a common practice to use air-mercury system for capillary pressure measurements. In the mercury method, the specimen is dried and placed inside a cell and then the cell is vacuumed. Subsequently, mercury is injected into the cell and the volume of mercury that enters the specimen at increasing pressures is measured. To apply the proper overburden pressure, a cylindrical specimen could be placed inside a confining sleeve and then the overburden could be applied. Figure 3.1 shows a simplified schematic of the mercury setup.

By measuring the displacement pressures for the assessment of WBE, seal capacity could be assessed from capillary pressure curves. However, there are some disadvantages associated with this method: it is a destructive test, it is performed on dried specimens which does not include fluid-surface interactions, and it may cause collapse of accumulations of grain surface coating minerals. In addition, the HSE issue related to mercury is a challenge. The advantages of the technique are that it is rapid and irregular specimens can be used in the case with no overburden pressure effect [6].

Porous-plate method—This technique can yield very accurate capillary pressure relationships. In this technique, a cylindrical specimen is saturated with water. A flat end of the specimen is then pressed against a flat porous plate, to make a good contact, in a cell filled with gas. The porous plate is also saturated with water. To improve the contact between the porous plate and the specimen, usually a moist tissue is placed between them. Subsequently, the gas pressure above the specimen is





increased in small steps to force the gas to displace the water from the specimen. In this procedure, the high displacement pressure of the porous plate allows brine from specimen to pass through but prevents the flow of gas. The specimen is removed at intervals and weighed until weight equilibrium is achieved. Considerable time may be needed, often a week or more, for each displacement step to reach equilibrium [7]. A diagrammatic sketch of this equipment is shown in Fig. 3.2.

Centrifuge method—Centrifuge measurements are more favorable as they take less time compared to porous-plate measurements; however, the measurements are not as quick as mercury measurements. In this method, a cylindrical specimen is saturated with water and then it is placed inside a centrifuge. Subsequently, it is spun in steps of increasing spin rate. The centrifugal forces force the water out of the specimen, replacing water with gas. There is a collector system for the drained water. The average saturation of water in the specimen, at each spin-rate, may be calculated from the volume of accumulated water and the porous volume of the specimen [8]. The capillary pressure distribution, at each spin-rate step, is given by [9].

$$P_c(r) = \frac{1}{2} \Delta \rho \omega^2 \left(r_e^2 - r^2 \right) \tag{3.2}$$

where r_e is the radius from center of rotation to the upper face of the specimen, r is the radial distance to any point in the sample, ω is the rotational velocity (rad/s), and $\Delta \rho$ is the density difference between displaced and displacing fluids.

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Property	Reservoir	Cap rock
Porosity (–)	0.125	0.05
Permeability (md)	2.028	1.11×10^{-3}
Irreducible water saturation (-)	0.3	0.66
Entry capillary pressure (psi)	0	39
Maximum capillary pressure (psi)	145	924

Table 3.2 Fluid flow properties for a reservoir and cap rock [10]

3.2.1.2 Permeability

Permeability is a property of the material, representing the ability of the material to transfer fluids. The WBE's permeability is the property controlling the movement and leak rate of formation fluids. As the rock permeability was first defined mathematically by Henry Darcy in 1856 [5], the equation that defines permeability in terms of measureable quantities is called Darcy's Law and is given in Eq. (3.3). Darcy's Law shows that permeability, k, is directly proportional to flow rate, q, length of the medium, L, and fluid viscosity, μ , and inversely proportional to cross-sectional area, A, and the differential pressure across the medium, Δp .

$$k = -\frac{q \cdot \mu \cdot L}{A \cdot \Delta p} \quad [m^2] \tag{3.3}$$

When a fluid with one centipoise viscosity and a pressure gradient of one atmosphere per centimeter of length flows with a flow rate of one cubic centimeter per second across a cross-sectional area of one square centimeter, the permeability is unity. For the units described above, k has been arbitrarily assigned a unit called Darcy in honor of Henry Darcy. One Darcy is a relatively high permeability as the permeabilities of most reservoir rocks are less than one Darcy. Therefore, the term millidarcy is normally used, where one millidarcy is equal to one-thousandth of one Darcy [5]. Table 3.2 presents example of fluid flow properties of a carbonate reservoir rock and a shale cap rock.

3.2.1.3 Acceptance Criteria for Fluid Flow Through Plugging Material

The goal of permanent P&A is to restore the cap rock in the wellbore or its functionality by placement of a plugging material across a suitable formation. Although the definition of a competent plugging material might be a matter of discussion, it is reasonable to consider properties of cap rock as the acceptance criteria for selection or design of any plugging materials. This adaptation is also valid for permeation characteristics of any plugging material as all existing materials, have some degree of permeability.

3.2.2 Bonding

Plugging materials should remain intact in place and block the migration of fluids. Therefore, sufficient bond strength and hydraulic bond strength of plugging materials with formations and steel are required. For zonal isolation purposes, hydraulic bonding is normally more important than bond strength.

Bond strength failure, debonding, may eventuate from two different loading scenarios; shear load, and tensile load. These loads can be induced by thermal cycling, hydraulic forces, volume changes of material, tectonic stresses, or a combination of these [11–13]. The volume change could be due to shrinkage and may occur either during curing or after setting due to changes in downhole conditions. Shrinkage of the plugging materials may impose sufficient tensile stresses on bonding between the plugging material and steel or formation to compromise the bonding. Another scenario that may result in tensile failure of bonding is the expansion of casing where the plugging material is placed inside the casing. When a reservoir starts to build up pressure underneath the plugging material, it may cause expansion of casing and consequently, *debonding* may occur. Debonding due to expansion of casing is predominantly for large casing sizes [2].

Hydraulic bond strength failure may eventuate from shrinkage or expansion of plugging material or expansion of casing caused by reservoir pressure build-up and/or due to interaction in the interface of casing and plugging material [14].

Bonding properties, bond strength and hydraulic bonding, are studied to improve knowledge and determine bonding ability of plugging materials. In 1962, Evans and Carter [15] published the result of their extensive study on shear bond and hydraulic bond strength of oilwell cement covering the effect of closed-in pressure, new mill varnish, uncoated pipe (wire-brushed, rusty, and sandblasted), dry pipe surface, and pipe surface being wet with either water-based or oil-based mud. Determining bond strength and hydraulic bonding of plugging materials considering effects of the above-mentioned factors are necessary.

3.2.2.1 Shear Bond Strength to Pipe

Shear bond strength defines the bond that mechanically supports pipe in the hole, and it is determined by measuring the force required to initiate pipe movement inside a sealing material (Fig. 3.3). The force is applied parallel to the contact surface [16]. This force when divided by contact surface area between the plugging material and casing, yields the shear bond [17].

Shear bond strength =
$$\frac{\text{Force}}{\text{Contact area}}$$
 (3.4)

The shear bond strength to pipe can be measured for two different scenarios; plugging materials placed inside the casing and plugging material placed outside the casing. The shear bond strength induced by a push-out test for cement outside casing is calculated by:

$$\tau_{av} = \frac{F}{\pi \cdot D_o \cdot L_c} \tag{3.5}$$

where F is the failure load which is applied on pipe, D_o is the pipe outside diameter, and L_c is the cement length. The shear bond strength of cement inside casing is given by:

$$\tau_{av} = \frac{F}{\pi \cdot D_i \cdot L_c} \tag{3.6}$$

where F is the failure load which is applied on pipe, D_i is the pipe outside diameter, and L_c is the cement length inside the pipe.

In one attempt, Evans and Carter studied shear-bond strength of cement to pipe [15, 17]. Variation between brands of API class A cements (see Chap. 4), curing temperature, condition of pipe, mud-wet and dry pipe, and closed-in pressure were factors studied by them. According to their results, there are correlations between compressive strength and shear bond on dry pipe. Closed-in pressure during setting of cement is detrimental to shear bond of cement to pipe after pressure is released. Shear bond strength is increased when cement is squeezed and wall pipe is waterwet. Mill-coated finish surface is detrimental to shear bond strength. It is important to mention that Evans and Carter applied both hydraulic and shear loads and therefore, their true measured hydraulic-bond strengths are uncertain. Table 3.3 presents shear bond strengths measured by Evans and Carter.



Fig. 3.3 Shear bond strength of cement to pipe **a** setup used by Evans and Carter [15], **b** setup used by Khalifeh et al. [18]

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Casing type	Time (Days)	Hydraulic bond (psi)	Shear bond (psi)
New	8 h	_	10
Used (rusted)	8 h	_	53
New	1	300	79
New (sandblasted)	1	500	123
Used (slightly rusty)	2	500-700	182
Used (wire brushed)	2	500-700	335
New (sandblasted)	2	500-700	395
Used (rusted)	2	500-700	422
New Pipe			
Water-based mud	2	175–225	46
Dry	2	375–425	284
Used (slightly rusty)		·	, ,
Oil-based mud	2	-	75
Water-based mud	2	_	174
Dry	2	-	182
Latex cement			
New	1	500	105
Used (slightly rusty)	1	360	58
	· ·		

Table 3.3 Examples of hydraulic- and shear-bonding properties of new and used pipe [15]

API Class A Cement

• Curing temperature: 80 °F

• Casing size: 2-in. inside 4-in.

• Cement-sheath thickness: 0.812-in.

Cement-pipe and cement-formation bond strength investigation shows that the bond strength depends on the nature of the contact surfaces and the cement hydration characteristics [16]. For a permanent plug, it is necessary to determine the appropriate bond strength for supporting the plug inside either openhole or casing and test it when the plug has set.

The shear bond strength to pipe is improved by use of expandable cement or bonding agents such as latex and surfactants. Expanding properties of expandable cements prevent the development of microannuli at the interface between casing and formation and cement plug, and subsequently, ensure good bonding with casing [19]. The inclusion of latex additives to cement slurry lowers the surface tension between the slurry and casing and helps cement adhere to casing while setting. Surfactants treat the oil-wet surfaces by removing oil and allow better bonding contact [20].

3.2 Functional Requirements of Permanent Well Barrier Elements



Fig. 3.4 Experimental setup for measuring tensile bond strength of cementitious materials to steel

3.2.2.2 Tensile Bond Strength to Pipe

Tensile bond strength is defined as the force which acts normal to the contact surface [16]. Tensile forces are applied perpendicularly to the contact surface of the supported specimen. Few publications are available for tensile bond strength to pipe and this area needs more attention [21]. Figure 3.4 shows an experimental setup for measuring cement-steel tensile bond strength.

3.2.2.3 Hydraulic Bond Strength to Pipe

Hydraulic bond is defined as the bond between pipe and cement, which helps to prevent the flow of fluids [15]. Hydraulic bond is determined by applying pressure at the pipe-cement interface until leakage occurs at either end of the specimen, Fig. 3.5.



Fig. 3.5 Test setup for measuring hydraulic bond test; **a** the used setup by Scott and Brace [22], **b** the used setup by Evans and Carter [15]

The hydraulic pressure when leakage appears is defined as the bond failure pressure. Studies conducted by different researchers [15, 17] show that pressures at which hydraulic bonding failure occur depends on the viscosity of the pressurizing fluid. Hence, the choice of pressurizing fluid is an important parameter which influences the breakthrough time and failure pressure. Therefore, gas bond tests and liquid bond tests should be considered for hydraulic bonding measurements. The gases could be compressed air, nitrogen, CO_2 , methane, etc. and the liquids could be crude oil and brine.

In 1966, Scott and Brace [22] studied the hydraulic bond strength at the casingcement interface for various conditions of the external surface of the casing, effect of mud film on the casing surface, effect of temperature on the resin-sand coated pipe, and effect of corrosive atmosphere on the resin-sand coating as important parameters. Table 3.4 shows the relative hydraulic bonding strengths of casing-cement interface with various surfaces measured by Scott and Brace.

Scott and Brace [22] found that excellent hydraulic bonding strengths are maintained at temperatures in the range to 350–400 °F. In addition, poor hydraulic bonding resulted from untreated pipe where mud film remained and surfaces which were millvarnished. However, resin-sand coating greatly improves the casing-cement bond. Figure 3.5 shows two different test setups used by different researchers for measuring hydraulic bond strength of cement to pipe.

In another effort, Evans and Carter [15] studied hydraulic bonding strengths of casing-cement (API class A cement) while measuring shear-bond strengths. Table 3.3 presents their results from these hydraulic- and shear-bonding tests. Evans and Carter investigated the effect of surface finish, drilling fluid, pipe size and length, cement-curing conditions, temperature and pressure on pipe, cement types, and the effect of

Surface condition	Surface coating	Hydraulic bonding (psi)
Dry	Mill varnish	<20
Mud film	Mill varnish	<20
Dry	Rusty	350-450
Mud film	Rusty	20–50
Dry	Acid-etched	250-400
Mud film	Acid-etched	40–50
Dry	Sandblasted	500–600
Mud film	Sandblasted	50–60
Dry	Epoxy coated, 6–12 mesh sand	700–950
Mud film	Epoxy coated, 6–12 mesh sand	500-600

 Table 3.4
 Effect of mud film on hydraulic bonding strength of casing-cement interface [22]

· Curing time: 24 h

• Curing temperature: 120 °F

• Cement type: not available

• Casing size: 4 ¹/₂-in. OD

squeezing. Their investigation concluded that the maximum reduction in hydraulic bonding is caused by a fluid layer at the cement-pipe interface; and hydraulic bonding strengths at cement-pipe interface are governed by surface finish of pipe, type of mud wetting, and degree of mud removal. In addition, they concluded that there is no fixed correlation between compressive strength and hydraulic bond strength to pipe. Low hydraulic bonding strengths at the cement-pipe interface are also a function of the pipe resiliency [15].

3.2.2.4 Shear Bond Strength to Formation

Shear bond strength of materials to formation depends on the nature of the contact surfaces and the reaction characteristics of the materials. Shear bond strength to formation maintains an intact barrier in place. Fluids only adhere to solids when the fluid wets the solid material and therefore, bonding of cement to formation is only possible if cement slurry filtrate is able to wet the wellbore wall. Roughness of formation surface, mineralogy of formation, degree of cement hydration, water-cement ratio, drilling mud and mud cake, downhole pressure and temperature, and types of cement to formation [16]. Figure 3.6 presents a schematic of the setup used for formation-cement shear bond strength measurements.

A study performed by Becker and Peterson on cement-formation bond shows that the strength of the developed bond between cement and formation is mainly due to wettability and the degree of cement hydration. In addition, contamination of cement slurry with drilling mud, oil, or gas strongly deteriorate the shear bond strength to



Fig. 3.6 Experimental setup used for formation-cement shear bond strength measurements



Fig. 3.7 Shear bond strength of cement with various rock types [23]

the formation. Therefore, contamination must be eliminated and mud or oil films on the formation surface should be removed totally. They also found that borehole temperatures up to 250 °F accelerate the development of shear bond strength. Higher temperatures can deteriorate the shear bond strength. However, the addition of silica flour can prevent the bond deterioration [16].

Opedal et al. [23] studied the role of formation type in the development of shear bond strength. A substantial reduction in shear bonding between cement and high porosity rocks (sandstone, limestone, and chalk) was observed in the presence of drilling fluid compared to the situation when low porosity shale was used as a formation. Existence of *Water-based Mud* (WBM) at the interface of rock and cement gives slightly better bonding than presence of *Oil-based Mud* (OBM) [15, 23]. Figure 3.7 presents the shear bond strength of some types of rock with and without drilling fluid film at the cement-formation interface.

When considering minimum shear bond strength (F_{sb}) required by a plugging material to avoid barrier movement, the resultant of two forces needs to be considered; reservoir pressure which pushes the plug upward and barrier weight and hydrostatic pressure above it, which act downward, Fig. 3.8. As a depleted reservoir may start to build up pressure after abandonment, it is safe to use initial reservoir pressure as the final reservoir pressure (F_R).

Cement-formation shear bond strength measurement—One of the main challenges in bond strength evaluation is lack of any standard procedure on how to perform the experiments. However, over the years, many researchers have followed the procedure implemented in the 60's by Evans and Carter [15, 17, 21]. In this method, a cylindrical rock sample is placed in the middle of a mold and then cement slurry is poured in the space between the rock sample and the mold, Fig. 3.6. The mold is covered with a plastic cover to avoid water evaporation during curing. Depending on the size of the test cell, the mold can be cured inside an autoclave to simulate downhole pressure and temperature.



It should be noted that the contribution of frictional force in real situations, at downhole conditions, is not identical to laboratory testing as washouts and other anomalies are not simulated in laboratory testing.

3.2.2.5 Tensile Bond Strength to Formation

Investigation of tensile bond strength of formation with any plugging material is an area which has not been studied so far. In this case, the applied force is perpendicular to contact surface; pulling the formation or the pipe away from the plugging material. The tensile bond strength helps to stop debonding created by lateral tectonic stresses.

3.2.2.6 Hydraulic Bond Strength to Formation

Hydraulic bond is defined as the bond between cement and formation, which helps prevent the flow of fluids [15]. The illusion of having similar cement-formation and cement-pipe hydraulic bonding strengths is one the reasons that few researchers have considered the cement-formation hydraulic bond strength measurement [15, 17]. Cement-formation hydraulic bond strength depends on the formation's mineralogy. Experimental works have shown that when cement is squeezed against a dry core, a higher hydraulic bond strength is attained [15]. Obtained hydraulic bond strength between cement and limestone shows higher pressure compared to obtained results for cement-sandstone, in identical circumstances. The failure path is also dependent

on formation mineralogy. When limestone is used as a formation, the failure path is at the formation-cement interface; however when sandstone is used as formation, the failure path is within the core rather than the interface. Presence of drilling fluid in the interface usually lowers the hydraulic bond strength, regardless of the formation type, compared to dry core situations. Therefore, drilling fluid displacement is important to be considered. Different types of mudcakes at the cement-formation interface influence the hydraulic bond strength differently. When the mudcake is fresh and soft, the failure pressure which cause leakage is lower than a situation where the mudcake is old and rigid. In fact, a rigid mudcake does not make a higher bond strength but as it is old and rigid, the mudcake has a higher resistance to flow. This phenomenon occurs in both sandstone and limestone rocks [15]. Generally, when cement is placed against a filter cake, the failure plane is within the filter cake and the flow path is at the filter cake-formation interface [24]. Usually, spacers and chemical washes are pumped ahead of the cement slurry for fluid separation and hole cleaning. Curing pressure has also an influence on hydraulic bond strength. As the curing pressure is increased, the hydraulic bond strength is increased.

Cement-formation hydraulic bond strength measurement—This type of test is accomplished by placing a formation core inside casing and pouring cement on top of it. Cement is allowed to set at the target pressure and temperature. An embedded pressure port on top of the setup provides the pressure for simulating downhole pressures, and the setup can be placed in a heating cabinet for simulating downhole temperatures. A pressure port embedded below the setup guides the applied hydraulic pressure across a predrilled hole along the formation rock to the cement-formation interface, as illustrated in Fig. 3.9.



Fig. 3.9 Hydraulic bonding to formation [15]

As there are no standard methods available on how to perform the bond strength measurements, different researchers select different loading rates which consequently influences the reliability of the data. Therefore, it is necessary to consider a realistic loading rate which may occur at downhole conditions.

3.2.3 Placeability of Permanent Barrier Material

The permanent barrier materials are going to be placed downhole and must therefore displace existing fluids. Hence, optimizing displacement and placeability processes of permanent barrier materials must be prioritized. Usually to minimize the instability at the interface between cement and drilling fluid, a spacer fluid is pumped ahead of cement slurry to separate it from drilling fluid. To remove drilling fluid and filter cake by use of a spacer, the force resulting from interaction between viscosity, friction, and buoyancy forces is the critical factor. In addition, the impact of rheological properties of fluids (i.e. yield stress and gel strength), physical and chemical effects must be considered.

To remove filter cake, the friction pressure introduced by displacing fluid (ΔP_{f2}) must be higher than the adhesion force between filter cake and formation (F_{fc}), Fig. 3.10. The filter cake removal is affected by rock permeability, pressure drop across formation and filter cake, properties of displacing fluid and filter cake, and velocity of displacing fluid [25, 26].

Although turbulent flow regime is noted as a solution for the removal of the drilling fluid and filter cake, achieving a turbulent flow regime for cement is challenging due to



Fig. 3.10 Spacer displaces filter cake when the differential friction pressure of fluids overcome the friction force between filter cake and formation

restrictions on fluid velocities. The rheological properties and chemical composition of spacers should be designed in such a way that a turbulent flow regime is achieved and as it should be compatible with the cement slurry, the spacer should have minimal effect on the properties of the cement [27]. It should be noted that a turbulent flow regime may cause a higher ECD and consequently, a higher risk associated with fracturing the in situ formation in open hole.

Downhole conditions dictate the plug placement techniques utilized but once the barrier material is placed, the placement operation needs to be verified. These operations are explained in Chaps. 7 and 9.

3.2.4 Durability

Durability means that the plugging material keeps its initial quality with respect to mechanical integrity and hydraulic conductivity. To assess durability of a WBE, aging tests are carried out in presence of fluids which represent the wellbore fluid at different life periods. If modification of macroscopic properties of plugging material occurs as a result of chemical evolution however it does not impair the mechanical properties of the material, then it is acceptable and not considered as harmful.

Available standards and/or guidelines address durability of sealing materials for production and abandonment periods together; however due to differences between the two periods of well life, the availability of comprehensive standards (testing procedure) or guidelines considering durability of plugging materials are necessary. The two major differences between production period and abandonment period are addressed as: mechanical loading scenario, and downhole environment [28].

Mechanical loading—During the production period, the stress variations caused by thermal and/or pressure changes are exerted on the wellbore and consequently on wellbore elements (e.g. casing, cement, and formation). When a well is depleted and permanently abandoned, the mechanical loadings still exist but the stress variations are slower compared to the production period.

Downhole environment—The nature of fluids in contact with plugging or sealing materials are different during production life and post-abandonment period. Consider a well which is operating under a sour gas re-injection process as the field produces high contents of sour gases. Hence, the exposure time and rate is different for the sealing material during the injection time of the well compared to its post-abandonment. Generally, the nature of chemical species and their thermodynamic state vary with time and type of well during production and post-abandonment [29]. Therefore, it is necessary to standardize the durability of plugging materials used for P&A considering well location, well type, and the thermodynamic state of chemical species.

Durability of a potential well barrier element is evaluated by considering its longterm behavior when exposed to different chemicals at downhole condition and at different time intervals, besides microstructure, volume, weight and permeability changes. In addition, the role and behavior of interfaces between plugging material and formation/steel caused by material deterioration, and role and behavior of interfaces between plugging materials and formation/steel caused by different mechanical loads and rates require consideration during the durability analysis.

3.2.4.1 Exposure Time

Well barrier elements selected in well barrier envelopes are supposed to maintain their integrity for a long time. NORSOK D-010 [1] suggests an eternal perspective for durability of well barrier elements. Nonetheless, the definition of long time is a matter of interpretation as an established definition has not been published. Some researchers have selected 1-, 3-, 6-, and 12-month time intervals as the exposure time in their studies [28, 30, 31]. However, it is recommended to continue for much longer periods, even up to 5 years [2]. Long-term testing can be useful for better understanding the properties of materials and material qualification for utilization as permanent plugging material.

3.2.4.2 Downhole Condition

Any material used in well barrier envelopes must be selected carefully to withstand downhole conditions. Bottomhole conditions include temperature, pressure, and formation fluids. In addition, geographical location of wells may also be a guideline for the selection of chemicals.

3.2.4.3 Chemicals

Well barrier elements of a permanently abandoned well experience chemical attacks from different chemical substances over a long period of time. The chemical substances include crude oil, brine, hydrogen sulfide, hydrocarbon gas, and carbon dioxide. Obviously, in a single well, a well barrier element may not be exposed to all of these chemicals after abandonment, hence, the chemical selection should be based on the chemicals present in the target reservoir. For instance, sour wells are common in the Republic of Azerbaijan and Russia. Therefore, the durability of WBEs in sour wells is a priority in these countries.

Crude oil—For performing aging tests, selected crude oils should represent the reservoir fluid. It is necessary to represent the chemical composition of crude oil and its density.

Brine—It is a common practice to prepare an artificial seawater as representative of brine. The most commonly used industrial standard for the synthesis of artificial seawater is ASTM D1141-98 [32].

Carbon dioxide—Materials may be exposed to CO_2 in gas state or dissolved in brine or crude oil (liquid state). The exposure scenario should mimic the formation

fluids. When CO_2 is dissolved in water, it is partly hydrated and subsequently carbonic acid is formed [33].

$$CO_2 + H_2O \iff H_2CO_3$$
 (3.7)

The formed carbonic acid dissociated in two steps:

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$
 (3.8)

and:

$$\mathrm{HCO}_{3}^{-} \leftrightarrow \mathrm{H}^{+} + \mathrm{CO}_{3}^{2-} \tag{3.9}$$

Formation of CO_3^{2-} changes the pH value of brine and the resulting pH is a function of the CO₂ partial pressure. CO₂ can corrode metal and deteriorate cement. In the presence of CO₂ dissolved in water, metal is unstable and as a result of the chemical reactions between carbonic acid and steel, Fe²⁺ is released:

$$Fe + 2H_2CO_3 \rightarrow Fe^{2+} + 2HCO_3^- + H_2$$
 (3.10)

When concentrations of Fe^{2+} and CO_3^{2-} ions exceed the solubility limit, the following reaction occurs and FeCO₃ precipitates:

$$\mathrm{Fe}^{2+} + \mathrm{CO}_3^{2-} \to \mathrm{FeCO}_3(\mathrm{s}) \tag{3.11}$$

The precipitated compound occupies a different volume compared to the initial compounds and it causes the casing to decompose.

High pH stabilizes the steel surface and prevents its corrosion but as explained, the pH of the medium is lowered due to dissolution of CO_2 in brine. Lower pH makes the steel surface unstable and rust is formed (see Eq. (3.11)). Formation of rust causes expansion and extensively deteriorates the cement [34]. Therefore, selection of steel as a WBE for permanent P&A might be a concern in long term.

 CO_2 deteriorates cement through two different mechanisms: carbonation and leaching. As presented in Eqs. (3.7)–(3.9), the presence of CO_2 in brine produces CO_3^{2-} , the formed ion reacts with Ca^{2+} and yields:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s) \tag{3.12}$$

The source of Ca^{2+} is supplied in two ways: the dissolution of $Ca(OH)_2$ broadly known as CH, and decomposition of hydrated silicate and aluminate phases or broadly known as calcium silicate hydrate (C-S-H) gel. The $Ca(OH)_2$ becomes unstable at a pH below 12.6 and Ca^{2+} is leached out and if the pH becomes less than 8, the strength giving C-S-H phases are destabilized and Ca^{2+} is leached out [35]. Taylor [34] explains the reactions as following:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$
(3.13)

$$xCaO \cdot SiO_2(aq) + zH_2O \rightarrow 2yCa^{2+} + 2yOH^- + (x - y)CaO \cdot SiO_2(aq)$$
 (3.14)

Taylor [34] showed that through decalcification of hydrated silicate and aluminate phases, new crystals form with smaller volumes and these crystals are a highly porous form of hydrous silica. The decomposition and formation of small crystals cause the deterioration of cement.

Hydrogen sulfide— H_2S is a corrosive material which is produced biologically (by the action of certain microbes) or geochemically (by the reaction of sulfurous minerals). The dissolution of H_2S in brine acidifies the medium and can attack steel and cement.

The electrochemical reaction of steel with H_2S undergoes a cathodic and anodic reaction. The cathode reactions are as follows [36]:

$$H_2S \to HS^- + H^+ \tag{3.15}$$

$$2HS^{-} + 2e \rightarrow 2S^{2-} + H_2$$
 (3.16)

The anodic reaction is the dissolution of steel and the formation of corrosion product [36]:

$$Fe \rightarrow Fe^{2+} + 2e \tag{3.17}$$

$$Fe + H_2S \rightarrow FeS_{1-x} + xHS^- + (2-x)H^+ + 2e$$
 (3.18)

This is an electrochemical reaction of H_2S corrosion which is known as rust. Corrosion causes enormous damage to tubulars and therefore, casing should be protected by a sealing material in order to be accepted as a permanent well barrier element.

 H_2S deteriorates cement through two major mechanisms: leaching and sulfidation [37]. As presented in Eq. (3.15), the acidic medium created by H_2S attacks cement and triggers the leaching of Ca²⁺ ions as follows:

$$Ca(OH)_2 + 2H^+ \rightarrow 2H_2O + Ca^{2+}$$
 (3.19)

$$3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 6\text{H}^+ \rightarrow 3\text{Ca}^{2+} + 6\text{H}_2\text{O} + 2\text{SiO}_2$$
 (3.20)

It has been proven that H_2S does not drastically decompose the neat cement sheaths but it does interact with the iron containing products of cement hydration such as ferrites to form sulfides; aluminates, and unhydrated di-calcium silicate components [37, 38].

Zhang et al. [39] studied rate of H_2S and CO_2 attack on pozzolan amended class H oilwell cement. Their results shows that that aqueous environment is more favorable

for H_2S to attack cement than H_2S in gas phase. In addition, they have shown that in aqueous phase, H_2S penetrates into the cement matrix more rapidly compared to CO_2 .

3.2.4.4 Microstructure Analysis

In the petroleum industry, quantification of mechanical properties of materials have been focused on and defined in different standards and guidelines. However, utilization of advanced technologies for quantification and analysis of material microstructure has not been recommended as much as it perhaps should be. Of these technologies one could address light microscopy, X-ray powder diffraction, Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM) which are vital for analyzing and quantifying microstructure of materials. It is necessary to study the microstructure of materials suggested as WBE over time and their modification at different conditions.

3.2.4.5 Volume Changes

A potential material to be used as a WBE should possess volume stability over time. Any degree of expansion may fracture the adjacent formation and any degree of shrinkage may cause microannuli and or debonding. The volume changes of a WBE may diminish the formation radial stresses and if it falls below the formation pore pressure, the risk of uncontrolled fluid flow is increased [31, 40]. Therefore, measuring the volume changes of well barrier elements as one of the durability parameters is vital.

3.2.4.6 Weight Changes

Degradation of WBE may lead to weight loss or weight gain. The weight change should not compromise the integrity of the WBE and other elements present in the well barrier envelope.

3.2.4.7 Permeability Changes

Any permanent plugging material should possess a very low permeability in the range of cap rocks and maintain the low permeability with an eternal perspective. Considering cement as a permanent plugging material, the permeability changes due to chemical attacks are caused by transformation of C-S-H phases to other phases. The newly formed phases are susceptible to occupying less volume or more volume. Therefore, permeability changes may occur [41].

3.2.4.8 Role of Material Degradation and Tectonic Loads on Durability of Interfaces

After a well is permanently plugged and abandoned, material degradation or induced tectonic stresses may create a small gap at the casing-cement or cement-formation interface, which is referred to as a *microannulus*. One of the processes which creates microannuli is called *debonding*, but it can also be created by residual drilling fluid. The microannulus creates pathways for fluids to escape. The risk of leakage through them is much higher than the risk of leakage through the bulk cement or corroded steel.

Studies show that alteration of the cement-formation interface is a complex problem which depends on rock type in addition to chemicals present in the medium. Theoretical and experimental investigations show that when cement is placed across stable shales in the presence of acidic brine (acidified by CO₂), Portland cement quickly adsorbs pore water present in the shale during the hydration process and after setting. This reaction changes pH of the acidic brine and makes it more acidic. The first and fast reaction which occurs is the dissolution of calcite whereas calcite present at the cement-formation interface has almost disappeared and a microannulus is created [42]. It should be noted that at downhole conditions, the dissolution process of calcite may be slower as the amount of acidified water is less compared to the laboratory case at which this study was performed.

The casing-cement interface is susceptible to degradation and hence, creation of microannuli in acidic environments. Studies show that when CO_2 finds a pathway across cement to steel it starts to degrade the casing-cement interface. Leakage of CO_2 accelerates the degradation of the interface [43].

When tectonic stresses are exerted on formation-cement or casing-cement, debonding may occur and consequently microannuli are created. This is due to differences in elasticity of the materials.

There are models to simulate casing-cement and cement-formation interface debonding. Most of these models are based on assumptions such as linear elasticity of casing, cement, and formation. These models also assume no cement defects at the initial condition [44]. Generally, these models are based on fluid-driven fracture propagation [45] and Coulomb friction [46]. All of these models are developed for well integrity analysis and modeling of cement interface debonding during the production life of wells, and not for permanently abandoned wells. It is therefore necessary to develop models addressing long-term integrity of casing-cement or cement-formation interfaces.

3.2.5 Reparability

The permanent P&A operation is performed to seal the potential fluid flow zones permanently with no intention of well re-entry. As, during the third phase of permanent P&A operations (discussed in Chap. 2), wellhead and conductor are removed,

there will be no access to the well for repairing any well integrity issue. Therefore, a candidate plugging material should withstand downhole conditions without compromising its sealing capability. There are some suggestions regarding self-healing or self-repairing materials whereby the material starts to heal itself if some defects are introduced over time. Self-healing cement products are one of these examples.

3.3 Qualification of New Plugging Materials

Any new plugging material designed for permanent P&A needs be qualified prior to being applied in the field. The qualification process may be based on a systematic approach including experimental work and theoretical analysis. The qualification process includes preparation of the material and its placement, verification of its intended functionality when it is in place, and its durability at downhole conditions. The qualification process needs to be quantitative and documented. All the possible failure modes need to be identified and analyzed based on the risks associated with the failure of its functionality over time. When the failure modes and their associated risks are considered, the failure modes are ranked based on the associated risk. Whenever laboratory testing is possible to be carried out, it needs to be performed. Confidentiality of the technology should not limit the availability of data required for qualification.

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