Overview of Tubular Goods in Thermal Recovery Technologies for Heavy Oil and Oil Shales

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Abstract

The materials selection for heavy oil and oil shale thermal recovery is of interest for recent oil shale technology development. The thermal recovery of heavy oil and oil shale is not only a traditional oil and gas upstream production process but also a precursor of refinery process. The challenges for the downhole tubular goods not only come from the reservoir conditions, but also come from the production process, i.e., the technique to deliver the energy, temperature and process chemicals introduced. This leads to the variants of oil shale technology, in turn, makes materials selection more difficult. There is clearly no "one-size-fits-all" solution.

In this report, the service conditions of various thermal recovery technologies are reviewed to understand the fundamental requirements for the downhole tubular goods materials. The most popular heavy oil and oil shale technologies, i.e., steam stimulation method, electromagnetic heating method, *in situ* combustion method, as well as close –recirculating methods are explored in detail. The history of materials selection, failure mechanisms under each technology is investigated for the insights of materials selection for *in situ* oil shale technology

Introduction

Thermal recovery technologies, such as steam flooding, fire-flooding, etc, are often used as oilfield tertiary oil recovery after primary production and water flooding (secondary recovery)it is the primary method used to recover viscous oil and oil-sands. These technologies are also widely explored for oil shale *in situ* retorting. The interest for the technology rises and falls with the fluctuation of crude oil price and environmental considerations. With a whole range of these unconventional oil recovery methods, few of which has been proven its commercially viability. Whichever way the oil is recovered the main aim of the operation is to transport the oil to the surface for further processing, this is carried out via the downhole tubing sitting inside the multi-layer of casing. Both casing and tubing are tubular good with different size. There are wide varieties of downhole tubular goods utilised in these thermal recovery technologies. The service environments are largely similar to the conventional petroleum production with the presence of hydrogen sulphide, carbon dioxide and chloride, etc. However, it can be more demanding for downhole tubular goods with high temperature, oxidizing atmosphere, increased sand production and novel cracking environments, etc. It is therefore a challenge to select the appropriate materials, manage the corrosion and integrity risks during the production. This paper is to therefore discuss the materials, service conditions and failure mechanisms in the heavy oil and oil shale thermal recovery industry.

Thermal recovery technology

The paper does not intend to discuss the details of heavy oil and oil recovery technologies in great depth. However the process condition will be briefly introduced that materials selection and failure mechanisms can be explored in the context. It is worth pointing out that all thermal recovery technologies are reservoir specific, there is no technique can be versatile across all fields. For example, Schamel *et al* has reviewed technologies for *in situ* recovery technology in

Utah USA [1] and demonstrated the applicability of the individual techniques that may be different even within a relatively small region (Table 1). This has to be kept in mind while materials selection for thermal recovery is being discussed. This somewhat increases the complexity when discussing materials selection issues.

Table 1 Applicability of Thermal recovery techniques in Utah

		Location					
		P.R. Spring Hill Creek	Sunny Side	Asphalt Ridge	White Rocks	Wonsits Valley	Tar sand Triangle
Thermal recovery Techniques	CSS	C	B	A	B	B	B
	SAGD	D	B	A	A	C	B
	Geothermal hot water flooding	D	D	D	D	A	D
	Electrical heating	C	B	B	B	D	C
	THAI *in situ* combustion	D	A	A	A	C	A

A: only moderate modification is required
B: major modification may be required
C: cannot be applied at the present time but worthy of further re-consideration in the future
D: The technology is considered to be unsuitable
CSS: Cyclic steam stimulation
SAGD: Steam assisted gravity drainage

An overview of thermal recovery technologies are illustrated in Figure 1. All have been classified as *"in situ"* oil shale technology, in which heavy oil and oil shale are heated underground and converted into syncrude and transported to the surface. Most of technologies involve hydro-fracturing process and the energy for the retorting process comes either from high temperature steam, electromagnetic energy, combustion or other sources. The categorisation in Figure 1 is largely based on the production conditions therefore the materials selection in the later discussion is based upon this specific category. Please note, however there is no easy way to generalise the materials selection issue regarding *"in situ"* thermal recovery due to the size and diversity of the subject at hand.

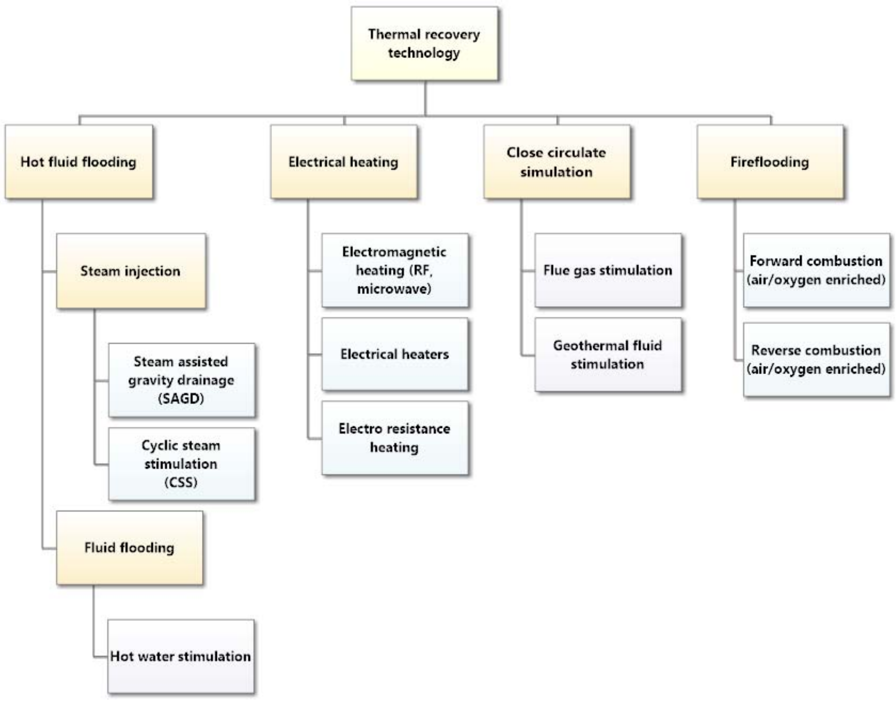

Figure 1 Overview of thermal recovery techniques for oil and oil shale from materials perspective

Tubular goods in heavy oil and oil shale thermal recovery

Tubular goods in thermal recovery have to survive the long term service, in which the synergic effects of temperature with corrosive environment may be there biggest challenge. In further discussion, we will categorise technologies based on service conditions, i.e., production temperature, inherent fluid corrosivity, etc. The materials selection issue will be addressed by corresponding category.

Other *in situ* technologies, e.g. *in situ* combustion, deliver energy underground burning. The process temperature is difficult to control precisely and the casing and other downhole tubular goods may suffer unexpected extreme temperature and oxidization atmosphere, which may not be experience in conventional oil and gas production.

Hot fluid (steam) flooding

Steam and water flooding are the typical examples of a non combustion extraction method. In this category, energy is delivered by a controllable way; in which retorting occurs under mild temperature range (normally less than 350oC). The corrosivity of the production fluid is introduced by reservoir geochemistry and potentially diluted by steam/water injected.

Two different stream stimulation methods, steam assisted gravity drainage (SAGD) and cyclic steam stimulation (CCS), have been used for decades as enhanced recovery of crude oil, oil sand and bitumen. Both are successful in commercial production of oil/tar sand with high reservoir permeability. The technology may be also applicable to oil shale *in situ* retorting. High pressure high temperature steam is injected into the deposit. The heat introduced by steam fractures the oil shale, and simultaneously converts it to syncrude. These methods are popular in oil/tar sand thermal recovery.

The SAGD process is illustrated in Figure 2, which incorporates a horizontal well pair using a production well near the bottom of the oil sand zone and a parallel steam injection well located 5 m above the production well. Oil sand between the well pair is heated by hot steams. Normally, the spacing of well pairs is 12 to 15m between the wellheads (Figure 3). Horizontal section extends to a further 200 to 1200 m. Each well pairs are expected to have 10-15 years of production life.

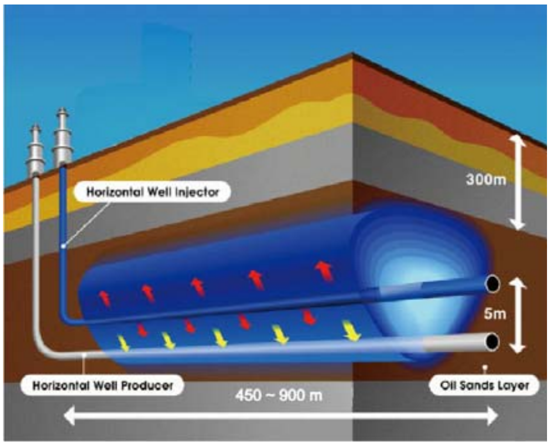

Figure 2 illustration of Steam Assisted Gravity

In initial heating stage, high temperature steam (200~300^{o}C) is injected from both wells. While the bitumen becomes mobile after a 3-6 months heating, the well pairs convert to production mode, i.e., the steam will only be injected through injection wells. Crude oil, steam condensate and formation water then drain into the lower lying production well by gravity and be lifted to the surface by natural steam lift or artificial lift. A non-condensable gas (NCG) potentially will be injected with steam to form a gas blanket to reduce the heat loss in steam chamber. Production well will be operated by 200~220^{o}C, which is

Figure 3 Halliburton SAGD wellhead surface layout

10~20°C below the steam saturation

The temperature of the stimulation process is carefully controlled and is below 350°C. Also note that there are no corrosive fluids introduced other than the steam and/or water, during the retorting/heating. The injection well integrity threat is therefore from the steam at elevated temperature and mechanical load. The major corrosion threat comes from the production well formation chemistry and its associates corrosivity in the

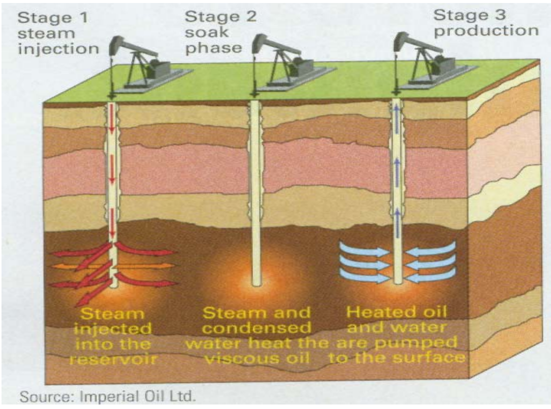

Figure 4 three stages of cyclic steam stimulation process [1]

retorting process.

The CSS process is slightly different however in so far as a single well operation via a "huff and puff" cycle. In "huff" stage, super hot steam is injected into well with high rate (200m^3/day, water equivalent) for short period of time (say, 1 month), following the shut-in for heat redistribution. In the "puff'' stage, the well is allowed to flow and later pumped for extended period (over 6 months). When the production rate becomes

A survey in Canada indicated that current casing design, which was using the above listed grade of steel, was sufficient to meet operational requirement. After 1980, the latter case design with casing grade N80, L80, J55 and K55 recorded 1 uphole failure per 1000 cycles steam injection and deemed to be extremely successful. [8] Current steel case such as J-55, K-55 and L-80 grade are not susceptible to SSCC

Reported casing mechanical failures include burst, collapse, tension, drill pipe wear, welding problems, thread damage, or leakage and perforation. Damage of telescoping and

temperature.

uneconomic, the whole process is repeated [3]. The oil recovery rate usually is low. Therefore, large number of wells is required for the commercial production. [4] CSS usually operates at pressures in excess of the reservoir fracture pressure with a asset life in the region of 25~30 years. [1],

The largest CSS operation in Canada is the Cold Lake project of Imperial Oil, which was commissioned in 1985 and has current oil rates of 150,000 bpd (with a peak rate of 540,000 bpd) from about 4000 active wells. The field is now mature and production is in decline after about 12 cycles over the past 20-25 years [1].

Materials selection for hot fluid (steam) stimulation

Downhole tubular goods need to service under elevated temperature for long time in steam flooding operation. Due to the low production fluid corrosivity, low alloy steel grades are the primary materials of the casing and other string. The common grades used in steam stimulation are API K55/J55, API L80/N80 grade. However, There are some operators using API grades P105; P110/C110 . Some steel making companies provide 55 ksi and 80 ksi grade proprietary steel for thermal applications, e.g. TN55TH, TN80TH from Tenaris. [5] In some even rarer cases, 316 stainless steel is used in the bottom horizontal section of production line of SAGD. (Please note the sizes of SAGD casing vary from 8-5/8 to 13-3/8 inch).

Failure history for steam stimulation

Although failure rates due to corrosion are relatively low and the grades used are reasonably reliable there are failures however. It was found that mechanical failure, coupling integrity, internal corrosion and cracking and erosion are the most common failure for casing in steam operation. [8]. This would suggest that the failures are more inclined t0 be from the user and not the environment.

buckling caused by thermal-linear expansion during steam injection is common in thermal wells. Curvature loading resulting from casing buckling and formation shear movement is also a contributing factor for thermal well

Connection failure is another category of failure for casing in steam operation. It was reported 80% of the uphole casing failure in thermal wells occurred at connections. The 2000 survey in Alberta suggested this trend continued. [4]. Leakage in couplings from cyclic thermal loading and excessive physical

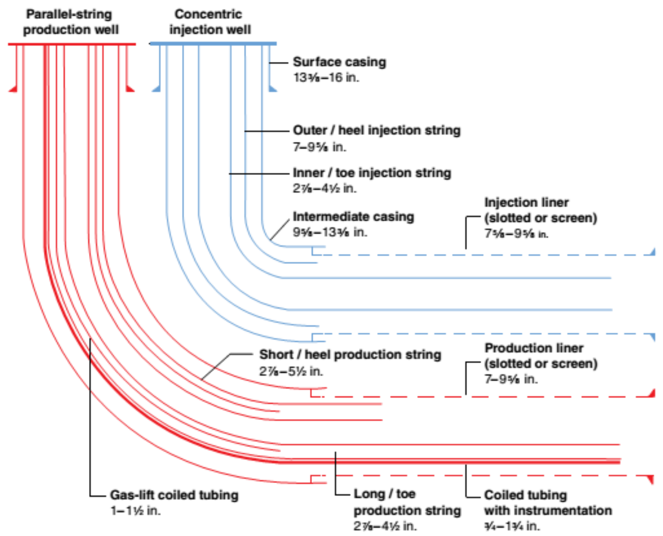

Figure 5 Example of casing materials in SAGD injection well [6] [7]

bending loads in dog legs seems a big threat of steam stimulation casing. [9]

Excessive thermal load is the also the cause for casing failure in steam stimulation. Cyclic

casing and connection integrity issue [4]

thermal loading with high thermally induced stress is anticipated in SAGD and CSS operation, which typically exceed the elastic limit of the material and cause the casing and connection to deform plastically.

During the injection stage, the thermal expansion of downhole casing and other strings is significant. Therefore, the materials with suitable thermal expansion properties should be selected. The temperature in production stage of CSS is significantly lower.

Creep is another cause of casing failure in steam stimulation where at high temperatures the metal component can slowly and continuously deform under load below the yield stress. The creep is a time dependent deformation which may eventually lead to rupture. Throughout cyclic process, there is strain hardening and/or strain softening, high temperature strain, aging creep and plastic tensile strain.[5]. In some casing design, API T95 grade has been utilised in the upper part of string (Note T95 is generally for use in sour condensate wells. Extensive hardness testing is required along with SSCC testing per NACE Standard TM-0177-Method A.)

Uniform or localised metal loss of carbon steel in an oil-water mixture depends on many factors, e.g. water cut, partial pressures of Carbon Dioxide (CO_2) and Hydrogen Sulphide (H_2S), temperature, flow velocity, flow regimes, etc. Generally, CO_2 (Carbonic acid) corrosion is the dominant mechanism of metal loss in the production fluid but any increases in H_2S levels, would also lead to increases in the general corrosivity of production fluid.

High temperature related metallurgical deteriorations, such as sulfidation, thermal fatigue, etc. are also of concern. Field experience would suggest that produced fluid in steam flooding is not as corrosive as it supposed to be thanks to the inhibiting effect of hydrocarbon and dilution effect of steam condensation. The coexistence of hydrocarbon is likely to mitigate the

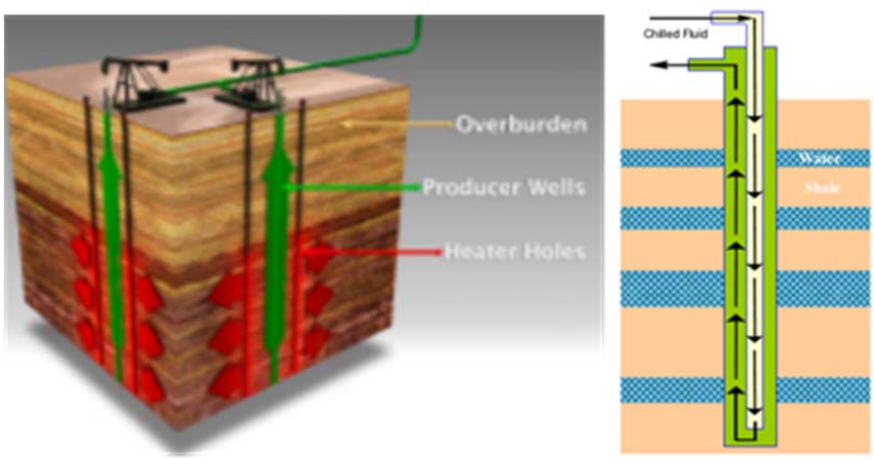

Figure 6 illustration of Shell's ICP process [13]

 WEBSITE: www.corrosionguru.com, E-MAIL: corrosionguru.com@gmail.com corrosion except at very low velocity in steam stimulation production. Experience suggests however that the corrosion rate is found to be exceptionally low even with high water cuts. SAGD field experience also shows no significant corrosion in SAGD emulsion stream. [10]. However the production lines may suffer erosion and flow assisted erosion / corrosion due to the presence of solids.

The removal of downhole sand screen may potentially increase recovery by 10%. However, it does aggravate the erosion in production wells.

Localized corrosion for the injection well is also identified due to existence of water condensation containing acidic gases on the inside surface of casing

Environment assisted cracking, such as caustic corrosion cracking and sulphide stress corrosion cracking maybe of the concern. Caustic corrosion cracking may be occur when carbon steel, low alloy steel and 300 series stainless steel exposed to caustic environment. Caustic breakthrough is often caused by the malfunction of steam generation and has been found at threads of tubular connection [11] [12]. Note: SCC maybe be of particular concern for susceptible low alloy high strength steel.

Sulphide stress cracking may be an issued and is associated with H_2S originating from formation underground. Microbial growth and make-up water and mild temperature may produce atomic hydrogen during the corrosion process which in turn may lead to atomic hydrogen induced cracking. [5]

The cracking tendency is higher between ambient temperature to 150^{o}C with blistering, HIC, and SOHIC damage have been found to occur between ambient and 150^{o}C or higher.

SSC generally occurs below about 82^{o}C (as per API 571), which is unlikely to be dominant in this production. However, chloride stress-corrosion cracking has been identified with 316 stainless steel components at the bottom of the production well Stress corrosion cracking (SCC) results from the combined action of three factors: Tensile stresses in the material, a corrosive medium (esp. chloride-bearing or hydrogen-sulphide environment) and elevated temperature (normally above 60°C for chloride-induced SCC).

Electromagnetic heating

Electromagnetic heating is another way of delivering energy in a controllable manner to retrieve oil shale. There are multiple trials utilising electromagnetic energy such as low-frequency electric resistive heating, higher-frequency radio-wave and microwave heating for the formation with low permeability. Typically, it takes 6 months to years to ramp the temperature up to a desirable level. The heating may also induce the micro-fracturing of the formation to enhance the syncrude recovery. This is particular popular in latest round of oil shale *in situ* retorting trials, such as Shell's In-situ Conversion Process (ICP), Exxon Mobil's electro fracturing, ET-DSP process.

Shell's ICP process is an example of electromagnetic heating process (Figure 6). Firstly, freeze holes are drilled 2.5 m apart to depth of target formation. The well will be recirculated with a chilled aqua ammonia solution (refrigerant), at an approximate temperature of -43^{o}C in the well. It may take up to 18 months to create an icy barrier to prevent the future groundwater contamination. In retorting stage, as heating occurs, the lighter and higher quality vaporized ICP products, plus steam and non-condensable gases, will flow to the producer holes. Because of the slow heating rate, and the close spacing between holes, the initial reservoir permeability required for fluid transport can be relatively low. There is no need to create permeability by hydraulic or explosive fracturing.

The production wells will collect the converted kerogen products (oil and gas mixed with some water) in the pyrolyzed zone and convey those products to the surface. The producer holes are drilled to a depth of approximately 510 m to the target formation. The heater holes will be drilled in the interior of the icy cooling containment zone, spaced approximately 7.5 m apart. Electric heaters will be installed in each hole to uniformly heat the oil shale. The approximate surface area of the heated pattern is 40 m by 30 m. The heaters are in place and heat the resource target zone for approximately 2 years to bring the average reservoir temperature to between 288~400°C.

The temperature of product from the producer holes will be approximately 205°C. The syncrude is quenched by water to cool the produced fluid. Quench water brought to the well head is mixed with the heated product coming from the producer hole. This results in a mixture of water and hydrocarbon mixture which is piped to the processing facility at about 120°C.

These processes are still in research and development stage with little or no public information available as yet regarding the materials selection for well casing. It is believed that Shell is testing heating elements without casing protection. Therefore, the selection for well casing and other tubular goods will be focused on producing wells. Under this production conditions, normal casing grade used for steam stimulation can be easily meet the requirements for Shell's ICP process.

Other technology may adopt different electromagnetic principles for energy delivery. However, the temperature seems always below 400°C threshold. For example, ExxonMobil using its patented Electrofrac® technology by squeezing the pulverised calcined coke/ graphite into the fracture to heat the whole fractured formation efficiently by creating electrical conducting paths, which will be served as heating elements in the further heating process. ExxonMobil's simulation suggested with 5 year heating, it

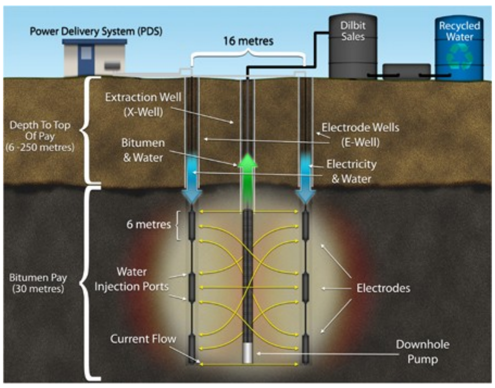

Figure 7 ET-DSP process [1] www.e-tenergy.com

may sufficiently convert 100m oil shale with a 40 m fracking spacing. For materials application point of view, casing may have to meet additional electromagnetic requirements (e.g. high Curie temperature, electrical insulation etc.) other than mechanical and corrosion resistance.

In situ combustion

In situ combustion was popular in 70s and 80s, which was also called as "fire-flooding" technique. In this process, part of oil/shale is burned in the formation through a controlled combustion. The heat from the combustion retorts the oil shale and converts it to

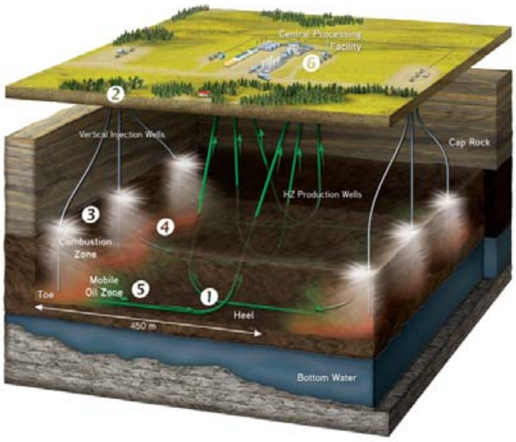

Figure 8 *In situ* combustion: THAI (Toe to Heel injection).

syncrude. Many companies developed their own variations based on combustion techniques and emerging new drilling technology. Either air or oxygen enriched air was utilised in underground combustion. There is no new research and development project for *in situ* combustion for oil shale retorting since later 90s. However, only a few commercial scale of projects are still running for heavy oil production around the world. [14]

Process description

So far, there is only forward combustion techniques been tried in field. The combustion was started near the injection well by firstly pumping air and/or oxygen into the oil shale formation by a dedicated injection wells. Kerogen and oil are ignited by gas burner, electrical heaters or pyrophoric chemicals. The combustion front is propagated by a continuous air (or air steam mixture). The combustion zone and retorting zone will be established between injection well and production wells depending on temperature profile. The heat generated from combustion zone applies to kerogen in retorting zone to release the crude oil and natural gas. Most of oil is driven toward the producers by a combination of gas drive (from the combustion gases), steam and hot water generated in the combustion. [15] Rather than an underground fire, the burn front is propagated as a glow similar to the hot zone of a burning cigarette. Some believed that combustion front is at around 430~650°C [16] while other believes the temperature is much higher. The temperature is sufficiently high for cracking and vaporizing the oil shale in the retorting zone which is downstream of the combustion front.

Using Toe to Heel Injection (THAI) process as an example, the materials selection for *in situ* combustion process can be discussed in several separated parts: 1) injection wells, in which air or other oxidant are injected; 2) production wells, in which syncrude and production fluid are collected and lifted to the surface; 3) special purpose well, e.g. temperature monitoring wells etc.

Materials service conditions

Produced gas compositions from different trials are listed in Table 2. Three phases flow (oil/water/gas) is obtained from production well The main constituents of gases are CO, CO_2, hydrogen sulphides, nitrogen, hydrogen, methane, oxygen and water. Minor species such as organic acid, NOx, SO_2 and oil condensate exist in there gaseous phase.

Low pH produced water usually comes with high level of dissolved solids such as chloride, organic acid, sulphates which forms the internal corrosive environment.

Table 2 Produced gas (dry base) from different trials [17]

Components	Paraho direct fired retort	Occidental vertical retort	Geokinetics horizontal *in situ* retort	Tosco-II retort
CH4	2.1	1.4	1.6	20.2
CO2	22.8	32.3	23.5	20.4
CO	2.5	0.9	8.3	3.4
H2	4.7	7.7	7.5	20.2
H2S	0.3	0.1	0.13	4.1
NH3	0.7	NR	0.06	Nil
O2	0.1	0.1	1.13	NR
N2	63.8	56.4	57.4	NR
H2O	20	38.3		20

The casing and other tubular goods may expose to extreme thermal and mechanical stress associated with high pressures, extremely high temperature (up to 1200 ~ 1700°c) for several hours in ignition stage (once burn front advanced, the temperature near the injection well may decrease.) The production casing part of casing may experience severe corrosion conditions such as oxidation, sulfidation and stress corrosion cracking. The wells must be designed to withstand the corrosive conditions by injection of stream and oxygen or air, and temperature of 200~400°C for long time operation. [18] The threat for the production comes not only from the nature of oil shale but also from the combustion process, in which high corrosive products are generated (Table 2)

The production well casing is at the original temperature for a long time the burn front moves more towards the horizontal rather than the vertical which can lead to a breakthrough. Once this happens, the production well temperature will increase steeply.

Thereafter, cooling is required for well integrity [3] i.e. to keep the bottom hole temperature (BHT) below the threshold. [19]. The bottom hole temperature of vertical section of production well is usually controlled below 250°C. Water injection was automatically started and maintained at a rate sufficient to keep temperature below that threshold.

The horizontal section of production well may well extend to the combustion zone and retorting zone, in which excessive temperature are expected. The produced fluid often contains unreacted oxygen. Excessive heat will require special, high-cost tubular to protect against high temperature corrosion. [15]. Well cooling is not possible therefore the temperature monitoring wellbore may deteriorate quickly in the path of burn front leaving the operator running blind.

In situ combustion materials selection consideration

In situ combustion trials in US for oil shale retorting are often short term with the well integrity and casing materials selection under serious scrutiny. However, the commercial scale trials in Russia suggested that a well life of 2-4 yrs is possible mainly based upon the correct materials selection. [20]

The materials of construction have a lot to contend with because as the combustion front moves gradually forward from the injection well to production well the temperature profile (mainly uncontrolled) and fluid corrosivity change accordingly. Therefore, the risk of the well casing exposure to extreme temperature is high. *In situ* combustion wells, both injector and producer, must take the thermal constraints and corrosion problems into consideration. The corrosion becomes much more severe in “in-situ combustion”, particularly with the oxygen enrichment technology. It is however possible to use non-exotic alloys for all of the production wellbore in fire flooding operation except across the zone of combustion, where nickel alloys has to be selected but this would take some time to finger print the exact corrosion profile.. [19]

Therefore forward combustion technique requires injection wells to be constructed to withstand extreme temperature especially during the ignition stage. However low alloy steel can have some limited success in air injection area. API 5CT N80 low alloy grade tubing has been used in India Oil and Gas Corp for *in situ* combustion but was found vulnerable in commercial production. Unsurprisingly It was identified that the low alloy steel is easily oxidised at elevated temperature in the presence of oxygen and water and that the tubing was severely corroded within 18 months of production and blocked by corrosion product.

This is particular serious in the ignition stage of forward combustion where the combustion front in the vicinity of the injection wells has temperature ranges of 400~600^{o}C are experienced.

For low alloy steel, the weight loss due to high temperature oxidization increased drastically and is unacceptable. [21]. However 7Cr-0.5Mo, 9Cr-1Mo showed negligible oxidization rates at temperature up to 680^{o}C. With martensitic stainless steel such as 11Cr and 13 Cr (API N80 grade) displaying better corrosion resistance at higher well temperatures.

Predictably Levy et al analysed a section of thermocouple well casing retrieved from Geokinetic *in situ* combustion where the casings were exposed to retorting temperature from 550~1100^{o}C. The casing material where of low carbon steel 1018. Even though the length of exposing time was unknown, the casing where severely damaged and deemed to be not fitted for service. [22]

Field pilot test in Canada showed similar experience whereby Clayton demonstrated that carbon steel, low alloy steel and Monel would suffer catastrophic corrosion damage.

Alloy s such as Incoloy 825, 904 Stainless Steel and Sanicro 28 experienced various degree of damage with only the Ni-Cr-Mo alloys containing at least 9% molybdenum such as Hastelloy C-276 and Inconel 625 surviving in the long term. [23].

Oxygen enrichment operation brings further challenge on casing and tubing materials of *in situ* combustion consequently both corrosion resistance and oxygen compatibility have to be considered in the materials selection.

For the resistance to “oxygen ignition” point of view, nickel based alloy such as Monel 400 and Inconel 600 are far more superior to stainless steel. Laboratory simulation test by Kohut indicated carbon steel and low alloy steel showed catastrophic behaviour whereas Incoloy 825 is acceptable if temperature is below 150oC. For temperature over 150oC Hastelloy C-276 and Inconel 625 will be the best candidate. Zawierucha's study found similar outcomes i.e. that Monel 400 is acceptable in oxygen enrichment operation up to 150oC and Incoloy 825, Hastelloy C-276 and Inconel 625 being acceptable candidates for oxygen enrichment operation up to 150oC and pH 4.0. He also suggested the molybdenum bearing Ni-Cr-Mo-Fe alloys are the best choice for this corrosive environment [23].

Austenitic Stainless steels such as SS 316 where severely corroded in the fire-flooding operation within reasonable short time exposures [22]. This is probably due to the extreme temperature in the temperature monitoring well, which could not be water cooled like the producing well t therefore lead to severe corrosion and disrupted the monitoring process.

There is little information regarding to use duplex stainless steel in in-situ combustion process this is probably due to some historical reasons and technical barriers. Firstly the second generation of duplex stainless steel 2205 with improved corrosion resistance was not widely used in oil and gas industry until 1980's whilst the most of *in situ* combustion retorting trials were already carrying out. Secondly, most of in-situ combustion trials have a short life; therefore, well integrity seems not a paramount concern for the trial. In some technologies, the well casing may be exposed to extreme temperature for short period of time during the ignition. Finally, there is concern for long term serviceability of duplex stainless steels under high temperature. (>300^{o}C)

The further study suggested that materials selection for *in situ* retorts must be based on their local environmental conditions and not on an overall definition of the type of corrosive environment which occurs in a retort [22]. The investigation also found one of the biggest variables will be the chemistry of formation water, which may bring different corrosion dynamics into the system. In this sense, each reservoir will be unique in corrosion perspective there is therefore no universal solution for materials selection apart from corrosion finger printing and correct material selection. [23]

Close circuit retorting

This technology is to heat the oil shale by delivering the energy in a closed circuit. The energy is either from artificial heating or from inherent heat, e.g. latent heat from geothermal fluid. CO_2, water, steam, flue gas [24], geothermal fluid, as well as special designed thermal fluid have been proposed as heat transferring media in different pilot projects.

Process introduction

In AMSO's (formerly known as EGL) Conduction, Convection, Reflux process (CCR) process , Superheated steam, geothermal fluid or Dowthermal are recirculated through the horizontal wells are drilled at the bottom of oil shale reservoir. As the kerogen warming up, it is broken apart and freed the oil and gas. In Chevron's CRUSH process, hot CO_2 was recirculated to heat the oil shale.

Materials selection consideration

The temperature of the stimulation process is well under controlled and it is normally below 400^{o}C. The stimulation fluid can be CO_2, saline water from geothermal production, flue gas from burners or specially designed heat transferring media. Since it does not physically contact with the formation, the threat for the production well mainly comes from corrosivity of formation in this retorting

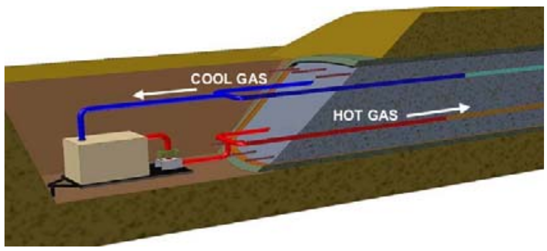

Figure 9 illustration of close circulating retorting [25]

process. Consideration of the process variables, materials and service condition should be similar to those of steam stimulation for the production well.

The corrosivity of heat transferring media and temperature are the primary concern of the materials selection for recirculating loop. Using geothermal fluid as an example, temperature of geothermal well is normally below 300°C. [26]

The corrosivity of geothermal fluid differs significantly by the geology location, aeration condition and mechanical designs. The difference in oxygen, pH, chloride, sulphide, sulphate, carbon dioxide, ammonia and microbial conditions may bring significance in both corrosion mechanisms and failure mode. [27]. There was a comprehensive study on the corrosion behaviour of metals in different geothermal fluids for materials selection purpose. [28]. It was found a much diversified results. In some location, carbon steel or low alloy steel may satisfy the purpose, while in other sites, nickel based CRA or titanium alloy seemed to be the only viable option. This highlighted the difficulty in generalising materials selection when dealing with geothermal fluids and other heat transferring media. In this application, where many of the variables such as velocity, metallurgical phase transitions and particular corrosive species may drastically alter the general corrosion rate. A site specific corrosion study should take all these factors into consideration based on the corrosivity of geothermal fluid as well as temperature. [29],

SAF 2507, SAF 2205 .Inconel 625, Nickel alloy [30], Copper based alloys and Titanium are potential candidates for the application.

Figure 10 Materials selection guideline [36]

Many laboratory and field test revealed the compatibility of the different alloys with geothermal hypersaline brines. [31]. The mixing bag of testing results suggested higher nickel content is preferred for SCC cracking and pitting resistance in alloy. Again, site specific corrosion study are required for the proper materials selection

With respect to the flue gas case, the materials selection has to be based on corrosivity of flue gas and corresponding corrosion mechanisms. [32] International Energy Agency (IEA)'s report on carbon capture and storage has outlined general concept on flue gas corrosion and guideline on materials selection.

Materials challenge in oil shale thermal recovery technologies

The casing and other tubular goods selection in this thermal recovery process may have to take the following criteria into consideration:

1) Mechanical strength and load at high temperature stability
   The well has to endure high temperature operation for extended period of time. In steam stimulation, up to 350 °C is expected. In fire-flooding operation, short term exposure to extreme temperature up to 1200oC is anticipated. Some section of the casing or lining may expose to elevated temperature for extended period of time
2) Corrosion environment
   The corrosivity is mainly from the oil shale formation. It may contain H_2S, CO_2, Cl in produced fluid. In fireflooding operation, residue O2 and other combustion product are also carried with production fluid. Therefore, more corrosive oxidizing environment is expected in *in situ* combustion production well.
3) Erosion resistance
   The thermal recovery usually comes with higher sand yield, which adversely increases the erosion and erosion corrosion rate.

The materials service environment for thermal recovery is largely similar to conventional oil and gas production, i.e., corrosive conditions, CO_2, H_2S, chloride, microbial growth, external casing corrosion, etc. Therefore, the requirements are also similar: mechanical strength, loads, stress.

It does come with unique requirement, in which temperature could be significantly higher. This may lead to the unique problems to be addressed, for example, differential expansion of the tubular goods; shear forces on the casing due to the swelling of the oil shale during process, as well as aggressive corrosion environment at elevated temperature.

Materials selection guideline

For steam stimulation with benign formation corrosion environment, it is proven that low alloy steel grade is sufficient. The common grades of Pearlitic and Martensitic steel such as API K55/J55, API L80/N80 grade are successful in both SAGD and CSS production. However there are some operators successfully using API T95, P105; P110/C110 grade. The low alloys steel grade includes C-Mn, Mn-V , Cr-Mo and Cr-Mn-Mo series. Martensitic steel grade includes 9-Cr and 13-Cr. Some steel making companies also provide 55 ksi and 80 ksi grade proprietary steel, e.g. TN55TH, TN80TH from Tenaris for improved thermal properties. [5]

High temperature corrosion resistance of austenitic stainless steel at 500~620oC were carried out for oil shale burning boiler environment with high chloride content. It was suggested that pearlitic-ferritic steel under 500-520oC should have at least 1.2~ 1.5 %Cr. For austenitic stainless steel service over 540°C, the Ni/Cr ratio should be great 1.0 to achieve better high temperature corrosion resistance. [33]

In the selection of materials for higher temperature service, particularly at temperatures above 371˚C, not only the corrosion rate of the material, but the effect that the temperature may have on the mechanical properties of the material must be considered. [34] The problem is much easier addressed if the temperature is the only concern during the retorting. Matthíasson etc suggested K55 to be utilised as production casing to case off the well down to the critical point (374°C at 22.1 MPa) for the well with Bottom hole temperature 550°C and bottom hole pressure is maximum 26.7 MPa. Creep resistant mateials such as API T-95 type 1 casing is utilised for top part of anchor casing. Even, K55 and L80 is selected, stress relaxation for K55 and L80 can be expected for temperature as low as 250oC [35]

The synergy of elevated temperature with inherent corrosivity is probably the biggest challenge for materials selection for oil shale technology. The associated issue includes novel cracking environment, severe erosion and erosion corrosion and troublesome galvanic corrosion by selection of different CRA.

Some individual companies provide their own guidelines on materials selection of tubular goods for oil and gas upstream application [37]. The general guideline for materials selection based on temperature and corrosivity is proposed by Special Metal Corporation (Figure 10). As a guideline, Inconel® 725 > Inconel® 725HS > Incoloy® 925 > Inconel® 718 > Monel® K 500 > Inconel® X750 > Inconel® 625 in corrosion resistance [38] However, the specific corrosive condition has to be studied carefully before the decision on materials selection can be made. For corrosion resistant alloy, the upper limit is usually 300°C.

There is no guideline available for iron based corrosion resistance alloy to be used in high temperature (>300°C). For example, Nickel institute's CRA selection guideline only goes up to 300°C for Alloy C 276 , 250°C for duplex 2205 and alloy 28, 200°C for austenitic stainless steel 316 [39]. Titanium alloys also had similar issues, for example, Ti-6Al-4V and Ti-6-2-4-6 appear to have the requisite corrosion resistance under HPHT conditions but very limited data exists to support this notion. Thus, considerable laboratory testing is still needed for titanium alloys as well as many of the current nickel base alloys under these more extreme HPHT conditions. [40]

Therefor for higher temperature, nickel base alloy will be the only possible option. Commercially pure nickel products have useful corrosion resistance up to around 538˚C. For severe corrosive condition, INCONEL alloy 600 is frequently substituted for Nickel 200 or Nickel 201.

Environmental stress cracking

The ferrous alloy for casing and tubing that must resist failure from environmental cracking. The tendency of sulphide stress cracking (SSC), as specified by NACE MR0175/ISO 15156, is low at elevated temperature range. The risk of chloride stress corrosion cracking for CRA, however, is significant at high temperature.

Balancing of mechanical strength and SSC resistance for low alloy steel is somewhat a dilemma as indicated by Craig *et al* [40]. At present, there is no easy solution for low alloy steels for this. The only acceptable alloys are high-strength CRAs such as martensitic and duplex stainless steels, nickel-base alloys, and titanium alloys. However, NACE MR0175/ISO15156 arbitrarily caps the service temperatures of nickel-base alloys and the duplex stainless steels at 230°C maximum

Martensitic alloys are susceptible to SCC by a hydrogen embrittlement mechanism. This susceptibility is strongly temperature dependent. It decreases with temperature from a maximum tendency at ambient to negligible at around 100 °C (210 °F). If the hydrogen sulphide level exceeds 0.03 atm, then 22Cr alloys should be used rather than 13Cr because of this risk. Hydrogen sulphide may be contained in the petroleum, or it may come from sulphate-reducing bacteria. This can convert a sulphide-free system become sour system after the fact and make initial materials choice. The 22Cr and 25Cr alloys have significantly higher resistance to chlorides and wet hydrogen For corrosion resistance above that furnished by super duplex materials such as the 25Cr alloys, super austenitic alloys fill a gap before nickel base alloys are needed. These alloys achieve a tenfold increase in hydrogen sulphide resistance and very high SCC resistance. These are the so-called 6Mo grades. [37]

Metallurgy of corrosion resistant alloy

Another important metallurgical concern for which little or no data are available is the potential for deleterious phases to form during long term well aging at temperatures in excess of 400°F (204°C), primarily for the CRAs. The aging of stainless steels and nickel-base alloys over 20 to 30 years of exposure may encourage the precipitation of phases such as Sigma, Mu, and Laves, which could lower fracture toughness and strength. Likewise, titanium alloys are expected to be susceptible to further aging under long-term exposure in HPHT well conditions, but with unknown results. [40] The formation of sigma phase precipitation usually happens below the sigma solvus temperature (590~950oC for SAF 2205). The sigma phase produced at low temperature is more damaging. The formation of sigma and chi phase results in the depletion of surrounding chromium and molybdenum. This leads to the detrimental effects on corrosion resistance. Other than that, the precise temperature control of the in-situ combustion is always questionable. Some section of casing and tubing may be exposed to elevated temperature during the normal production up to 500^{o}C. This is typically detrimental for high alloyed duplex stainless. Normally the upper service temperature of duplex stainless steel is limited to less than 300^{o}C. Exposing to temperature over the limit promotes the secondary phases such as alpha prime phase over the time, which leads to severely embrittlement known as 475^{o}C embrittlement (885^{o}F embrittlement). [37]

Nickel alloy is not immune to this as well. Some nickel alloy, e.g. Nickel 200 may subject to Intergranular embrittlement by graphite when held at temperatures of 426-760˚C for extended periods of time. Nickel 201 is not subject to such embrittlement, [34].

Conclusion

The materials selection for heavy oil and oil shale thermal recovery is an ongoing task. The thermal recovery of heavy oil and oil shale is not only a traditional oil and gas upstream production process but also a precursor of refinery process. Therefore, materials selection has to take both processes into consideration. The challenges for the down-hole tubular goods not only come from the reservoir conditions, but also from the production process. The variants of oil shale technology have aggravated the situation for materials selection. There is clearly no one-fit-all solution.

Low alloy steel is a low cost option. It can be used in oil shale thermal recovery as long as the production fluid in reservoir is not severely corrosive. Both SAGD and CCS in North America are using various grade of low alloy steel in oil sand recovery. They are deemed to be extremely successful materials in these two methods. Mechanical strength in high temperature, coupling integrity, and resistance to environmental cracking are the most demanding attributes for the application. For the materials using in the electromagnetic heating, other than mechanical and corrosion resistance requirements, electromagnetic requirements (e.g. Curie temperature) for the particular technology has to be evaluated.

For *in situ* combustion technology, low alloy steel may be selected for injection wells and vertical section of production well as long as the wellbore temperature can be well controlled. However, the damaging mechanism of the wells exposure to short period of extreme temperature is noted. For the casing contacting with combustion zone and retorting zone, e.g. horizontal section of the production well and temperature monitoring wells, exotic heat resistant alloy, i.e., nickel based alloy and titanium alloy may have to be selected.

For the technology involving geothermal fluid, the Corrosion resistant alloy (CRA) to be selected has to withstand the geothermal fluid at high temperature. It is not only from the natural constituents of the fluid, but also the process condition, in particular the aeration and oxygen ingression.

Ultimately, it is the user's responsibility to determine the acceptability of an alloy for a specific production field and thermal technology. A material selection for a specific application is based on field experience, laboratory testing results and cost analysis. A detailed process analysis with detailed information of production fluid corrosivity is required before the proper materials selection can be made. This is not only crucial to materials selection but also important for future corrosion management and well integrity management. [41]

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