INNOVATIVE SOLUTIONS FOR SULPHUR IN QATAR

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ABSTRACT

The estimated sulphur output from Qatar by 2012 is around 4 Mtpa \(^1\). Qatar Shell is using novel technologies to utilize sulphur in applications such as concrete (Shell Thiocrete) and asphalt (Shell Thiopave). Shell Thiocrete is an innovative modified sulphur binder that completely replaces the cement and water in concrete. In 2008, the first field trial of sulphur concrete tiles was installed in Ras Laffan Industrial City (RLIC), Qatar. Laboratory results showed that the bending strength of all the sulphur concrete mixtures was greater than the bending strength of the cement concrete (control). The laboratory water absorption result of the sulphur concrete tiles was also lower than that of the cement concrete tiles.

Shell Thiopave is a technology that enables a portion of the bitumen in an asphalt mix to be replaced by modified sulphur, resulting in a pavement that has enhanced mechanical properties such as increased stiffness and significantly reduced permanent deformation. A trial to compare the performance of Shell’s sulphur-modified asphalt with conventional asphalt mix was conducted in 2007 through the construction of test sections of a two-lane road at RLIC, Qatar. The performance of the test sections was assessed through a field monitoring study on December 2008 and May 2009, which showed that both the conventional and sulphur-modified asphalt were free of any moderate or major distresses.
INTRODUCTION

Shell has many years experience handling sulphur and exploring new ways to exploit its natural properties. One of Shell’s main goals is to create a virtuous circle of sulphur management: removing sulphur where it adds little value (e.g. in fuels), and then using this recovered sulphur to add value somewhere else (e.g. as a component of new end-products with significant benefits over traditional products of a similar nature. By applying its leading-edge technological expertise, Shell has developed the Thio technology that successfully bring the benefits of sulphur to a range of applications such as in concrete (Shell Thiocrete*), in roads (Shell Thiopave*), and in fertilizers (Shell Thiogro*).

The development of Qatar’s large gas resources, particularly the North Field, will increase its sulphur production significantly (1). The North Field is only moderately sour (0.5-1.0% H2S) but combined with the sheer scale of operations planned, the forecast is a volume of 4 million tons per annum by 2012 (equivalent to almost 12,000 tons/day of sulphur) (1). Projects that Shell is developing with Qatar Petroleum - the Pearl GTL (Gas-to-Liquids) project and the Qatargas 4 LNG (Liquefied Natural Gas) facility - will contribute to the production of the elemental sulphur in Qatar and Shell is committed to finding novel applications for the sulphur produced. In both the GTL and LNG processes, sulphur has to be removed in the feed gas processing operation. In the GTL process, which is a technology that converts natural gas via a chemical conversion over a catalyst into a range of products such as naphtha, kerosene, diesel and lubricant oils, the catalyst is very sensitive to sulphur poisoning and virtually all sulphur needs to be removed in the gas treating step. In the LNG process, the sulphur has to be taken out to avoid freezing out of H2S and consequently blocking the main cryogenic heat exchangers that cool natural gas to liquefied natural gas. Also, the aluminium linings of LNG carriers can be quickly corroded by H2S.

There is a combination of factors that suggest that Shell sulphur concrete and sulphur-modified asphalt could become important innovative construction products in Qatar. Firstly, the construction industry in Qatar is growing, resulting in a high demand for construction materials.

Thio is the Greek word for sulphur.
* Shell Thiocrete, Shell Thiopave and Shell Thiogro are trademarks of the Shell Group of Companies. Hereafter Shell Thiocrete concrete will be referred to as ‘sulphur concrete’, and Shell Thiopave as ‘sulphur-modified asphalt’.

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This growth creates an opportunity for construction materials based on Qatari natural materials as long as these comply fully with Qatar Construction Standards. In 2005, it was reported that the construction sector and real estate sector in Qatar formed 5.7% and 2.3% respectively of the gross domestic product (GDP)\(^2\). This has been reflected in the increased consumption of cement as presented in Figure (1)\(^5\). As presented in Figure (1), the annual forecasted consumption of Portland cement in Qatar will be around 8.5 million tons in 2011.

![Figure 1: Portland cement consumption in Qatar \(^5\).](image)

Moreover, there is a tremendous growth in transportation infrastructure. The Public Works authority in Qatar, Ashghal, is implementing 60 major road projects by 2012 with reported associated costs greater than QR25bn \(^3\). In the next five years, Ashghal plans new road projects worth around $20bn to be carried out in Qatar \(^4\). However, due to the high temperatures in Qatar, especially during the summer season, roads in Qatar are susceptible to permanent deformation in the asphalt layer of the pavement as presented in Figure (2). Permanent deformation, also known as rutting, occurs primarily due to reduction in the shear strength of an asphalt mixture at high temperatures; and consequently, the loss of the mixture’s ability to resist shear stresses exerted by repeated traffic loading. Sulphur-modified asphalt

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\(^5\) The historical consumption data is from GOIC data base (IMI), actual production + net imports. The forecasted data (2007-2012) is based on a growth rate of about 19% \(^5\)
could be applied in Qatar, as it will use sulphur, a locally produced material, to improve shear strength of the asphalt mix and construct superior roads with enhanced resistance to permanent deformation.

![Figure 2: Permanent deformation in a road in Qatar.](image)

Secondly, the manufacturing process of conventional concrete utilizes significant quantity of potable water for mixing and curing processes, which puts demand stress on the scarce drinking water resources in Qatar. It is forecast that annual water consumption for concrete production will be 3 million tons in Qatar by 2011 (5). According to the Qatar construction standards (QCS) (6), the mixing water temperature of concrete shall not be more than 25°C. During the long summer months in Qatar (May through September), the temperatures can reach up to 50°C (7). Thus, ice as per the QCS is crushed and used as a replacement of water for mixing of concrete. Moreover, it has been documented that elevated concentrations of chloride and sulphates salts, present in the coastal areas of the Arabian Gulf (e.g. Qatar), causes concrete deterioration due to reinforcement corrosion, sulphate attack and salt weathering (8). Figure (3) highlights the degradation of conventional concrete products due to exposure to seawater in Qatar. In addition, sulphur concrete has a lower carbon footprint than Portland cement concrete since the emissions associated with limestone conversion in the
Portland cement manufacturing process are avoided. Thus, as well as being able to cut the use of water and cement in Qatar, sulphur concrete can also offer high strength and water/acid resistance with a lower carbon footprint.

QATAR SHELL RESEARCH AND TECHNOLOGY CENTRE (QSRTC)

Qatar Shell Research and Technology Centre (QSRTC) was established in 2005, with the official opening of its permanent facilities at the Qatar Science & Technology Park in April 2008. In February 2009, the state-of-the-art laboratory was inaugurated. Shell has made a US $ 100 million commitment to the QSRTC to be spread over ten years. QSRTC has been established

* Actual CO₂ savings will vary by location and application.
to align through the science park Shell’s technology programme to Qatar’s needs. The work at the Qatar Shell Research & Technology Centre is focused on the development and implementation of technologies that support Qatar’s energy industry, particularly Qatar’s aspirations to be the globe’s largest liquefied natural gas exporter and the gas to liquids capital of the world. QSRTC focuses in three main elements, namely, carbonate research (e.g. subsurface and outcrop modelling of the Khuff formation), gas research (e.g. co-products of the GTL process such as sulphur) and learning.

The sulphur utilization programme in QSRTC is part of a global research and development effort to develop Shell’s sulphur concrete and sulphur-modified asphalt technologies, with particular emphasis on the needs of the Gulf region. In addition to Qatar, sulphur research is carried out in various locations within Shell, such as Canada, USA, The Netherlands, The UK and India. Both Qatar Shell New Business Development (NBD) and QSRTC are providing commercial and technical support, respectively, for the research and development of Shell sulphur concrete and development of sulphur-modified asphalt in Qatar.

USE OF SULPHUR IN CONCRETE PRODUCTION

References to the utilization of sulphur, both modified and unmodified, as a binder for concrete date back to the early 1920s. Early concrete prepared with unmodified sulphur had serious durability problems especially when subjected to repetitive cycles of freezing/thawing, humid conditions and/or water immersion (9). Failure of unmodified sulphur concrete was reported to be due to internal stresses set up by changes in the crystalline structure upon cooling (10). During the 1960s, various endeavours were attempted to improve the quality of products made of sulphur concrete by using additives for sulphur modification. The development of modified sulphur to prepare concrete enhanced the feasibility of using sulphur in preparing durable construction products. Various attempts have been made since the 1970s to commercialize the production of concrete with modified sulphur. However, due to either technological or economic reasons, this type of concrete has always been used in niche applications such as industrial laboratory floorings and pickling tanks.
Shell Sulphur Concrete

Shell sulphur concrete technology uses an innovative modified sulphur binder that completely replaces the cement and water in concrete. This technology has the potential to take sulphur concrete from use in niche applications such as chemical flooring to more mainstream applications such as garden products, road construction products (e.g. pavers, curbstones and traffic barriers) and marine products. This is because the relatively low cost of the modification technology allows sulphur concrete to be considered in applications previously covered only by Portland cement. Table 1 presents the indicative material properties of sulphur concrete and mortar. Sulphur concrete has a range of benefits such as:

- The manufacturing process for sulphur concrete generally has a lower carbon footprint compared to that of Portland cement concrete.
- No water required in the manufacturing process for sulphur concrete.
- Faster setting and final strength development.
- Superior strength properties.
- High resistance to acid and salt-water.
- Excellent surface finish and pigmentation.
- Very low water pickup property due to the hydrophobic nature of sulphur concrete.

Table 1: Indicative material properties of Shell sulphur concrete concrete/mortar

<table>
<thead>
<tr>
<th>Description</th>
<th>Technical info.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive Strength</td>
<td>40-60 MPa</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>10-17 MPa (3 point bending test)</td>
</tr>
<tr>
<td>E modulus</td>
<td>35 – 40 GPa (measured in compressive mode)</td>
</tr>
<tr>
<td>Porosity</td>
<td>&lt; 0.2%</td>
</tr>
<tr>
<td>Water Absorption</td>
<td>&lt; 0.1% (14 days total immersion)</td>
</tr>
<tr>
<td>Creep Strain</td>
<td>0.13% after one year at 20 ºC (sulphur bound concrete)</td>
</tr>
<tr>
<td>Expansion coefficient</td>
<td>Estimated range 8 x 10^-6 to 10 x 10^-6 per ºC (Sulphur bound concrete)</td>
</tr>
</tbody>
</table>

\[ All values are for use of Shell Thiocrete as a mortar unless otherwise specified. \]
Sulphur concrete is suitable for many of the same applications as Portland cement concrete and precast units are installed in the same way. However, the manufacturing process utilizes a hot mixing process similar to that used to manufacture asphalt for road construction. Sulphur concrete is a thermoplastic material \(^{(8)}\) made of modified sulphur, coarse aggregates (e.g. rocks and gravel), fine aggregates (e.g. sand) and additives (e.g. pigments for coloured concrete).

Sulphur concrete can be tailored to the specific needs of different concrete applications, enabling precast manufactures to produce high strength, durable products. Precast sulphur concrete products are based on combining established asphalt mixing technology and precast moulding techniques and has the following advantages:

1. High mechanical strength
2. Better utilization of moulds
3. No long curing period
4. Low leaching- extending the range of aggregates suitable for concrete manufacture
5. Freeze-thaw resistant
6. Lower embodied CO\(_2\) compared to Portland cement concrete
7. Reduced need for admixtures
8. Colour retention and efflorescence free

Due to the melting point of sulphur (120\(^{\circ}\)C), sulphur concrete should only be used in non-structural applications. However, in its target applications the melting point of sulphur is an advantage as it enhances the recycling opportunities for sulphur concrete. Trials to confirm the commercial recycling processes for sulphur concrete are currently underway. Shell’s development work to date indicates that sulphur concrete will be suitable for recycling in three ways:

- By crushing, reheating and reforming to produce new concrete products with Shell modified sulphur as the binder.
- By crushing and grading- to produce aggregate that can be used to make cement-bound precast products.
- By crushing and grading- to produce aggregates that can be used as bound or unbound road base materials.
**Sulphur Concrete Activities in Qatar**

The sulphur utilization Research and Development (R&D) program within QSRTC incorporates an array of activities, viz.:

- Pigmentation experiments, which encompasses a wide range of coloured sulphur concrete capitalizing on the much wider and more vivid colour pallet obtainable with sulphur concrete. Figure (4) presents some examples of the range of coloured sulphur concrete.

![Figure 4: Example of range of coloured sulphur concrete.](image)

- Prototyping a wide range of construction products such as paving bricks, I-blocks, curbstones and tiles. Figure (5) shows some of the sulphur concrete products.
- Design mix optimization using Qatari local materials such as dune sand.
- Utilization of by-products of other industries present in Qatar.
- Sulphur concrete recycled aggregates in cement bound precast products. Figure (6) presents aggregates from recycled Shell sulphur concrete products.
- Testing physical (e.g. water absorption), mechanical (e.g. unconfined compressive strength) and environmental (e.g. leaching) performance of the different design mixes.

QSRTC and NBD are working in close cooperation with Qatar General Organization for Standards and Metrology in order to certify sulphur concrete products in Qatar. Arrangements are now underway to bring into Qatar a mobile sulphur concrete batch plant capable of demonstrating the technology as well as developing products. Furthermore, the sulphur utilization team within QSRTC is collaborating with various regional and international research institutes and entities in testing and assessing the performance of sulphur concrete.
Figure 5: Sulphur concrete products such as:
(a) Paving Bricks, (b) I-Blocks, and (c) Tiles.

Figure 6: Aggregate from recycled
Shell sulphur concrete products.
The first field trial of sulphur concrete in Qatar was performed in May 2008. QSRTC and Shell Global Solutions installed a 16 square meter area of sulphur concrete tiles in the Pearl GTL Worker's Village. This site is located in Ras Laffan Industrial City (RLIC), Qatar. Figure (7) shows the installed sulphur concrete chessboard. These tiles were produced in the Netherlands through cooperation with Shell Global Solutions and a Dutch precast concrete manufacturer. The tiles were evaluated at a Dutch certified laboratory in accordance with NEN-EN 1339, which is the EU standard used to classify the performance characteristics of cement concrete tiles. The evaluation encompassed both the mechanical (i.e. bending strength) and weathering resistance (i.e. water absorption) properties.

The performance of the sulphur concrete tiles was compared to those of ordinary Portland concrete tiles (control). Laboratory results showed that the bending strength of all the sulphur concrete mixtures (11.6 – 14.3 MPa) was greater than the strength of the cement concrete (7 MPa). Moreover, the water absorption of the sulphur concrete tiles (<0.2% m/m) was lower than that of the cement concrete tiles (0.7% m/m).

Figure 7: Shell sulphur concrete chessboard after installation.
USE OF SULPHUR IN ROAD CONSTRUCTION

The technology of using sulphur in roads was developed in the 1970s and was originally known as sulphur extended asphalt (SEA). There is a wealth of information published about the properties of sulphur-modified asphalt road sections constructed in the 1970s and early 1980s (11). Laboratory and theoretical studies from the US Federal Highway Administration indicated that the addition of sulphur to asphaltic pavements could produce better, more economic pavements (12). In spite of the improvements in road mechanical properties, the change in sulphur and hydrocarbon economics as well as environmental concerns related to the handling and safety of molten sulphur meant that SEA became an unattractive option. In the early 2000s, however, interest in the use of SEA mixes was renewed by innovations in sulphur technology that eliminated hazards associated with molten sulphur use.

Shell Sulphur-Modified Asphalt

Shell sulphur-modified asphalt is a patented asphalt mix additive technology, for sulphur-enhanced road construction, developed by Shell Sulphur Solutions since 2003. It is added to the asphalt mix as solid pellets with a diameter less than 5 mm. It is added at ambient temperature and quickly melts in the mix to form part of the binder as it comes into contact with the hot asphalt mix. Figure (8) shows the Shell sulphur-modified asphalt pellets. In general, bitumen contains a very small amount of natural sulphur, however, some of the added sulphur-modified asphalt pellets acts as a bitumen extender, whilst the other portion of the added sulphur-modified asphalt pellets forms a lattice structure that gives the improved mechanical properties.

Figure 8: Shell sulphur-modified asphalt pellets.
This technology enables a portion of the bitumen in the asphalt mix to be replaced with sulphur and special additives, resulting in a pavement that has enhanced mechanical properties such as increased stiffness and significantly reduced permanent deformation in the asphalt layer of a pavement particularly at high ambient temperatures. The increased stiffness is attributed to the fact that as the warm asphalt mix cools, the special blend of sulphur and additives in the sulphur-modified asphalt pellets form a strong lattice within the bitumen matrix. Moreover, the special additives have been combined with sulphur to minimize the creation of fumes during mixing, transportation and paving.

The benefits of using sulphur-modified asphalt are realized in terms of extended road life and/or thinner pavements. It also works effectively across a wide range of climatic conditions. In hot climates, where locally available bitumen can be too soft to give the desired road life, using sulphur-modified asphalt mixes can be used to stiffen the asphalt mix. The increased high-temperature stiffness and shear strength of the sulphur-modified asphalt mix (a) enables softer, high penetration bitumen to be used effectively in hot climates, (b) improves the overall structural capacity of the road, and (c) increases the road’s resistance to permanent deformation. These enhanced properties of roads constructed using sulphur-modified asphalt have been demonstrated under real field conditions in case studies in the USA, Canada, China, France, India and Saudi Arabia.

Furthermore, sulphur-modified asphalt enhances asphalt pavements’ resistance to fuel spill damage, which shorten the lifespan of pavements by breaking down the binder in the asphalt mix. Fuel immersion tests give a clear indication that using sulphur-modified asphalt significantly increases the capability of asphalt mix to withstand contact with fuel, helping to ensure that roads achieve their projected service life. Figure (9) illustrates the superior fuel resistance of sulphur-modified asphalt than that of the conventional asphalt mix when immersed in JetA1 fuel for 24 hours and in diesel after 28 days. Sulphur-modified asphalt pellets have a higher density than bitumen, thus in order to have an optimum design mix, a formula is used to calculate the mass of the pellets that must be added to the mix to keep the overall binder volume the same as conventional mix. Typically, the optimal ratio of bitumen to sulphur-modified asphalt pellets in the binder respectively lies somewhere between 70:30 and 60:40.
Sulphur-Modified Asphalt Activities in Qatar

A field trial section of sulphur-modified asphalt mixture was laid at Pearl Village, the worker accommodation for the Pearl GTL project in RLIC, Qatar. The construction commenced in October 2007. Figure (10) shows the laying of the sulphur-modified asphalt mixture in RLIC. A 600-m section was constructed using sulphur-modified asphalt followed with a 300-m section of conventional asphalt mixture. The bitumen was 60% by mass and the sulphur-modified asphalt pellets was 40%. The sulphur-modified asphalt mixtures had about 25% less bitumen mass than the conventional mixture. Sections of the roadway were constructed using both materials i.e. sulphur-modified asphalt and conventional, it consisted of two lanes with a base course thickness of 8 cm and a wearing course thickness of 5 cm. It is estimated that these test sections will experience about 1,500 bus passes daily in each direction. For a design period of 10 years, the estimated traffic loading is between 0.7-1.5 million Equivalent Single Axle Loads (ESAL). QSRTC has signed a research collaboration agreement with Texas A&M University at

Figure 9: Cores after Fuel immersion test in
(a) Jet1 fuel for 24 hours and (b) Diesel after 28 days.
Qatar to monitor and evaluate the performance of the field trial road stretch (i.e. asphalt mixtures containing sulphur-modified asphalt and conventional hot mix asphalt).

![Image of asphalt paving]

*Figure 10: Sulphur-modified asphalt mix laydown in RLIC, October 2007.*

The results of the field monitoring study showed that the total road section (sulphur-modified asphalt and conventional) was free of any moderate or major distresses such as longitudinal cracking, transverse cracking, permanent deformation or potholes \(^{13}\). The laboratory characterization of sulphur-modified and conventional asphalt mixtures showed that the sulphur-modified asphalt mixture exhibited better resistance to permanent deformation and higher stiffness than the conventional mixture. Figure (11) shows typical appearance of permanent deformation (rutting) resistance test specimens after 8000 wheel load applications of sulphur-modified asphalt in comparison to conventional asphalt mix.

The stiffness of the two mixes was compared using the indirect tensile stiffness module (ITMS) test at temperature ranging from 10\(^\circ\)C to 40\(^\circ\)C(50\(^\circ\)F to 104\(^\circ\)F) in order to determine the stiffness ratio\(^v\). These results show a general trend of an increased stiffness ratio when using sulphur-modified asphalt that is particularly evident at high temperatures. Figure (12) presents the ratio of increase in stiffness with the addition of 40% by mass sulphur-modified asphalt.

\(^v\) Stiffness ratio: defines as the ratio of increase in stiffness that the sulphur modified asphalt has over conventional mix.
pellets. Furthermore, industrial hygiene monitoring during laying operations showed that SO$_2$ and H$_2$S emissions remain below the maximum limits when the temperature is controlled to be less than 145°C.

![Figure 11: Typical appearance of permanent deformation (rutting) resistance test specimens After 8000 wheel load applications.](image)

![Figure 12: Ratio of increase in stiffness with the addition of 40% by mass Shell sulphur-modified asphalt.](image)
Since this field trial, a new and improved Shell’s sulphur-modified asphalt technology has been developed. This new sulphur-modified asphalt technology allows the asphalt mix to be manufactured at a lower target temperature of 130°C, which falls into the ‘Warm Asphalt Mix” category. The use of low temperatures in road construction means reduction in energy consumption during construction. Thus, future trials in Qatar will incorporate this improved formula.

CONCLUSIONS AND RECOMMENDATIONS

The sulphur utilization programme in QSRTC (Qatar Shell Research and Technology Centre) is part of a global research and development effort to develop Shell’s sulphur concrete and sulphur-modified asphalt technologies, with particular emphasis on the needs of the Gulf region. Both sulphur concrete and sulphur-modified asphalt can have a potential market in Qatar.

Shell technology reduces the cost of modifying sulphur for use in concrete enabling Shell to offer manufacturers a sulphur concrete binder at a price that is competitive to Portland cement. This revolutionary breakthrough means that the performance advantages and positive environmental impacts of sulphur concrete, which have long been proven in niche applications, can now be accessed on a much wider basis. Unlike traditional cementitious binders that rely on chemical bonds being formed when they react with water, sulphur concrete uses modified heated liquid sulphur to “glue” the aggregate together and form a stable, hard concrete product. The first field trial of sulphur concrete in Qatar is a 16 square meter area of sulphur concrete tiles in the Pearl GTL Worker’s Village, Ras Laffan Industrial City (RLIC), Qatar, laid in May 2008. Laboratory results showed that the bending strength of all the sulphur concrete mixtures was greater than the strength of the cement concrete. Moreover, the water absorption of the sulphur concrete tiles was lower than that of the cement concrete tiles.

Shell sulphur-modified asphalt is a technology for sulphur-enhanced asphalt mix developed by Shell Sulphur Solutions since 2003. Shell’s technology enables a portion of the bitumen in the asphalt mix to be replaced with sulphur and special additives, resulting in a pavement that has enhanced mechanical properties such as increased stiffness and significantly reduced

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permanent deformation in the asphalt layer of a pavement particularly at high ambient temperatures. A trial two-lane section of roadway of asphalt mix containing sections of Shell sulphur-modified asphalt and conventional asphalt mixture was constructed in October 2007 at Pearl GTL Worker’s Village, RLIC, Qatar. The results of the field monitoring study showed that the total road section (sulphur-modified asphalt and conventional mixture) was free of any moderate or major distresses. Industrial hygiene monitoring during laying operations showed that SO$_2$ and H$_2$S emissions remain below the maximum limits when the temperature is controlled to be less than 145°C. The laboratory characterisation showed that the sulphur-modified asphalt mixture exhibited better resistance to permanent deformation and higher stiffness than the conventional mixture.

ACKNOWLEDGEMENTS

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REFERENCES


