DEPLETED HYDROCARBON RESERVOIRS PRESENT A SAFE AND PRACTICAL BURIAL SOLUTION FOR GRAPHITE WASTE

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Abstract

A solution for graphite waste is proposed that combines reliance on thick impermeable host rock that is needed to confine the long-life radioactivity content of most irradiated graphite with low capitalistic and operational unit volume costs that are required to render this bulky waste form manageable. The solution, uniquely applicable to irradiated graphite due to its low dose rates, moderate mechanical strength and light density, consists in three steps: first, graphite is fine-crushed under water; second, it is made in an aqueous suspension; third, the suspension is injected into a deep, disused hydrocarbon reservoir. Each of these steps only involves well mastered techniques. Regulatory changes that may allow this solution to be added to the gamut of available waste routes, geochemical issues, availability of depleted reservoirs and cost projections are presented.

1. INTRODUCTION

Most irradiated graphite wastes contain significant activities in radioisotopes with half lives longer than 30 years, a figure widely considered a marker for "long life" classification and subsequent routing. At the time reactors reach their final shutdown, graphite activities range from 1 to 1000 Bq/g ^{36}Cl and ^{41}Ca; from 1 to 1000 kBq/g ^{14}C and ^{63}Ni.

Such "long-life" levels generally do not warrant irradiated graphite a classification as Low Level Waste as would otherwise its low content in harmful isotopes ^{60}Co, fission products and actinides. Indeed the projected health impact to the most exposed individual of the public from the mobile fraction of the former isotopes, through the hundreds and thousands years of diffusive transport time allowed by their very slow decay, threatens, when considering graphite disposed of in surface or shallow repositories, to exceed the internationally accepted [1] 0.3 mSv/year limit and a fortiori lower limits set for long-life waste by national regulators and waste management agencies.

The logical outcome is for graphite waste to be disposed of as Intermediate Level Waste in so-called geological repositories made of horizontal galleries bored in clay or hard rock ca 500 m underground. Due to the great volumes standing in obsolete nuclear facilities, the expected cost for so doing might reach in the order of several billions euros and pounds for France and the United Kingdom. Utilities' financial provisions for nuclear dismantling are not fully adequate to such expenses.

On the technical side it should be noted that, since engineered barriers cannot be reckoned to retain their mechanical integrity and even their chemical buffer effect over very long times, the superior protection against labile long-life isotopes afforded by geological repositories rests entirely on the thick low-diffusivity, low-permeability rock formations that host them.

Considering that the soft mechanical properties and low gamma emission of irradiated graphite make it a rather easily handled material, this leads to the proposal of reworking it for disposal in natural equivalents of geological repositories, indeed in the deepest and tightest geological traps, tested over geological eras that are hydrocarbon reservoirs.

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The idea of using these for unwanted waste is not new: a depleted natural gas reservoir, the ”deeper Lacq” formation in Southwest France, has been serving since 1975 as a ultimate repository for liquid waste from local thiochemistry, pharmaceutical, cosmetics and caustic industries.

It should be noted that Lacq’s is a different approach to the injection of liquid radioactive waste in shallow saline aquifers that was carried out both in the United States and in Russia, since the Lacq reservoir is both much deeper and naturally confined.

Issues arising when considering a similar repository for irradiated graphite waste in slurry form are regulatory, political, scientific and technical. They are reviewed in the following paragraphs.

2. REGULATORY ISSUES

Regulatory issues are examined in this paper with France as an example.

Deep burial of dangerous material in France is governed by Article L 515-7 of the Code of the Environment, which begins as follows in its latest version (2006): *Burial of dangerous materials of any nature in deep geological layers is subject to the authorisation of the administration. This authorisation (...) may be prolonged for an unlimited duration, on the basis of an ecological evaluation comprising an impact assessment and the exposition of solutions alternative to the continuation of the burial and of their consequences (...). The dispositions of the present article do not apply to the burial of radioactive waste.*

By exception, the injections of chemical waste in “deeper Lacq”, run by an industrial venture owned by the Total group and named “Cretacé 4000” after the host geological layer and its depth in meters, are since 2003 authorized by the Prefect of the French department of Pyrénées Atlantiques under the 84th and last article of the law Nr 2003-699 *relative to the prevention of technological and natural risks and damage reparation*, last modified in 2010, that stipulates : *Notwithstanding all contrary dispositions, the injection of industrial effluents in the geological structure designated as Crétacé 4000, located in the Lacq region (Pyrénées-Atlantiques) may be authorised, following advice from the Higher Board on Prevention of Technological Risks, provided the operator of the injections demonstrates by a safety study on the long term that they are innocuous for the receiver matrix, notably vis-à-vis its natural confinement*.

A similar devolution of authorising power to the local ‘department’ cannot be envisaged for radioactive waste, which is since 1991 addressed by distinctive laws. Regulation governing irradiated graphite waste remains yet in the limbo where it was placed by the law Nr 2006-739 *relative to the sustainable management of radioactive matter and waste*. This law prescribes *the elaboration of burial solutions for graphite and radium-bearing wastes so that the repository may begin operation in 2013*. Although the text has not been amended, dispositions taken late 2012 designate June 2015 as the moment when alternative solutions must be identified. Barring this, says the law : *final radioactive waste that cannot, for safety or radiological health reasons, be disposed of in surface or shallow repositories are buried in a deep geological layer*, by which is meant *the disposal in an underground facility specially prepared for this purpose in conformity with the reversibility principle*.

For graphite waste to be disposed of through any route ‘alternative’ to the now called CIGEO ‘specially prepared’ facility, France therefore needs a new law or an amendment to the 2006 law.

It should be noted that French regulations do not explicitly prohibit the disposal of radioactive waste as liquid or slurry. Nevertheless ANDRA, the nuclear waste agency, requires waste to be solid for it to be accepted in any of the agency’s disposal facilities. Also, absent legal clarification, the ‘retrieval’ clause that applies to waste disposal in the CIGEO facility might be construed as forbidding injection in hydrocarbon reservoirs as proposed here.

To be licensed to operate a French graphite injection facility an organisation shall presumably unite ANDRA’s expertise in handling nuclear waste and anticipating rock-waste interaction with that of the oil and gas industry in running injections and monitoring reservoirs and that of the power industry in handling coal slurries.

The example of the legal situation in France thus suggests that, in order for irradiated graphite injection in depleted hydrocarbon reservoirs to be allowed, interested nations should pass legislation that:

- designate the administrative body in charge of receiving the demonstration of innocuity and delivering the authorisation to operate (most properly the nuclear regulator);
- determine the operating licensee (eg. the nuclear waste agency or a special organisation);
- wave for this waste type post-injection retrieval requirements; and
- spare it from prescriptions that ultimate radioactive waste be disposed of as solid.

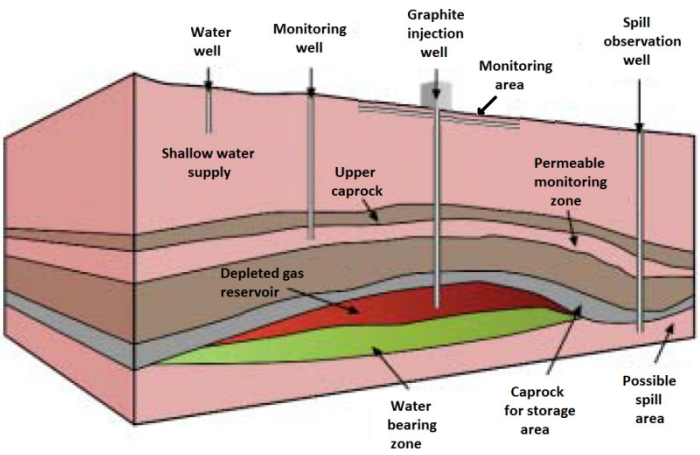
3. TECHNICAL ISSUES

Industrial experience that can be drawn on for graphite injection includes power generation using water-coal slurries as fuel. Black coal (the purest and less porous type of coal, eg. anthracite) indeed possesses physical, mechanical and microstructural properties quite similar to those of irradiated graphite. Water-coal slurries, prepared by wet grinding of coal, are pumped through pipes to the burner. Their solid matter content can be up to 80 wt%. The slurry exhibits some colloidal behaviour that contributes to prevent disaggregation throughout transportation. Added ionic surfactants charge particles negatively, which provides a repulsive force and prevents agglomeration.

Injecting solid suspensions in cracked and porous rock through kilometre-long pipes is nowadays a matter of routine for the oil and gas drilling industry. Calibrated sand particles, up to 2 mm in diameter, most notably used for hydraulic fracturation, will settle in the host rock where they become trapped.

It is not, though, to be expected that milled graphite behave exactly as calibrated sand for its particulates are of irregular size and shape, the material absorbs water to some 15 wt% and is not so hard as silica. On the other hand deep injection will require a much longer pipeline than coal slurries. Nevertheless this combined experience suggests that milling characteristics, surfactant additive and pumping power might be with some ease adjusted for irradiated graphite to be properly transported to the depleted reservoir and to settle in its undamaged porosity.

Best practices in these fields should be identified and adapted to the purpose. Particular care should be devoted to ensuring the leak-tightness of the injection well, which is the main point where the biological environment and shallow underground, including fresh water aquifers, might become contaminated. Technical solutions feature double-wall piping and post-operational sealing using proven, inert materials, eg bentonite. The wells formerly used for the exploitation of the hydrocarbon reservoir must be similarly sealed and checked before graphite injection is allowed.



Schematic representation of i-graphite injection in a depleted gas reservoir

Spillage beyond the lateral perimeter of the reservoir is not expected since hydrocarbon exploitation will have either greatly reduced its original pressure (in the case of a reservoir with a bottom seal like 'deeper Lacq' where the pressure fell from 480 bar to 30 bars) and henceforth the graphite injection won't prime it back in any significant measure, or raise the lower aquifer, which graphite injection won't by far sink back to its pre-exploitation level.

Monitoring for the spread of leached radioelements and radioactive gas, as will be required by the national nuclear regulator, leads to sensor wells being drilled above and around the reservoir. Probes inserted there should screen beta emissions from gamma and alpha ones, single out the looked-for spectra of ^{14}C and ^{36}Cl among those of ^{40}K and other natural emitters, and in addition withstand local pressure, chemistry and temperature conditions and relay the information to the surface.

4. SUITABLE RESERVOIRS

Although saline aquifers are not altogether unsuitable for the disposal of irradiated graphite, their enormous volumes and relative proximity to the surface (less than 1000 m) make them more appropriate for carbon capture and storage (CCS) schemes.

On the contrary depleted hydrocarbon reservoirs should be preferred as repositories for irradiated graphite since capacity is not an issue there: capacity of Crétacé 4000 is about 850 Mm^3 with an injected volume of chemical waste ca 120 000 t/year [2]; in the Paris basin the CCS capacity of hydrocarbon reservoirs has been reckoned to be about 100 Mtons; the smaller oilfields in the latter region, which have been yielding a few thousand tons a year each since the 1970s-1980s, are showing signs they are past their peak.

After reservoirs become exhausted, turning one of them to graphite repository would make excellent use of the proven confinement properties of such natural formations throughout the Cenozoic era. Besides, their residual hydrocarbon content will dilute any organic radioactive carbon released from graphite.

Seismic analysis will be used to ascertain the overall structure of the reservoirs, their heterogeneities and boundaries, and check there is no retrievable oil and gas left in any significant amount.

Hydrocarbon reservoirs may lie deeper than mid-depth saline aquifers most suitable for CCS. The "deeper Lacq" formation in the Aquitaine basin and the Donnemarie field in the Paris basin lie respectively 3500-5000 m and 2500 m below ground [3]. Similarly configured hydrocarbon reservoirs can be found in the London and Yorkshire basins [4]. Extra depth provides trapping and sealing power for leached radioelements.

As learned from experience, site selection should include such cultural parameters as the presence of a public familiar with industrial risk and willing to accept its benefits and drawbacks. This plays to the advantage of sites with a history of oil and gas extraction and in need of a substitution activity, in contrast to those involved in agriculture, where a pristine-looking 'terroir' (growing territory of a given product, such as cheese or wine) has an economic value the neighbourhood of a nuclear waste facility may jeopardise. In this essential regard far-depth will be seen also as a soothing feature.

5. DEPOSITION AND TRAPPING PROCESSES

While the rheology of suspended particles has been the object of numerous experimental and theoretical studies, the hydrology of two-phase flows in porous media is a more recent field [5][6]. Modelling the porous network and its evolution through the graphite deposition process, based on in-situ tests and lab analyses and experiments carried out under representative pressure and temperature conditions, will allow optimising the suspension characteristics and the injection parameters so that the graphite particles will neither clog the vicinity of the injection point, nor spread over a wider area than necessary.

A number of samples retrieved from host rocks at times of oil and gas exploration are available (taken care of in France by the 'Institut Français du Pétrole') for such investigations. They show most hydrocarbon reservoirs to be made of dolomite $CaMg(CO_3)_2$.

Graphite particles won't chemically interact either with this porous matrix or with the caprock. They will settle in the former at some distance from the injection point owing to decrease in fluid velocity, and there stay put most likely forever.

The choice of surfactants should ensure that leached radioelements do not combine in chelants while in suspension. Instead, numbering in irradiated graphite in weight parts per million, they will react with the hugely greater mass of host rock. It is expected that chlorine, leached as an anion, will bond to the dolomite matrix, while nickel and other cations will become physically sorbed on the negatively charged porous surfaces or may enter the chemical dolomitic complex.

Gaseous ^{14}C release as CO and CO_2, the latter possibly hypercritical under the physical conditions, is expected to form structural dolomitic carbonate, whereas ^{14}C-bearing CH_4 should be trapped under the caprock, get vastly diluted in the residual natural gas and ultimately undergo isotopic exchange.

If the chosen host rock is not calcitic or dolomitic but made of, for example, sandstone, its trapping properties may appear less favourable. Such rocks nevertheless usually contain enough calcium carbonate cements for the chemistry to be helpful.

Reaction processes should, like settling patterns, be experimentally verified in labs and modelled. The resulting data will inform the demonstration of innocuity.

Release risks from minor seisms of the type that occur around depleted hydrocarbon reservoirs are expected to safely be disregarded thanks to the solid nature of graphite particles and the strength of radioelements bonding with to host rock, except for methane, some release of which might occur, were a crack to arise in the caprock, strongly mitigated by the high negative gradient pressure and diffuse.

6. COSTS

Injection of chemicals in the "deeper Lacq" repository has been reported to being billed to producers by the Total group at about 10 €/ton [7], which can be presumed to represent the marginal cost.

Rousse 1 (Total S.A.)

A better reference for the whole graphite injection venture should be the CCS injection pilot operation in a neighbouring 4500 m deep formation (known as 'Rousse 1') with an injected CO_2 amount (51 000 tons [8]) standing in the same league as graphite wastes inventories. Expenses there were 60 M€ capitalistic and 10 M€/year (over 3.2 years) operational [9], which makes 1.8 k€/ton, not including post-operational surveys.

We assume the cost for graphite injections to be quite similar to that for the pilot CCS, since both include investigative testing, modelling and making the demonstration case, initial survey, interacting with stakeholders and the public, well equipment and sealing, pumping, and monitoring during and after the injections. Further investment was made on request of the locals (noise reduction and landscaping). Part of the CCS project, an existing gas-fuelled plant that provided steam and power to the local industry was turned to oxycombustion, which involved changing the burners and installing a cryogenic oxygen generator; we reckon capital investment for this to be in the same order as that of a graphite crushing and suspension making plant. On the maintenance side, piping a graphite suspension should not be more complicated and incident-prone than piping hypercritical CO_2.

Graphite injection is therefore expected to compare very favourably on price with the service to be rendered by France's CIGEO ILW section: expenses there, in large part incurred from the process of drilling kilometres-long, 6 to 8 m-wide galleries in compact clay at a depth of 500 m, put the disposal cost for blocked and packaged waste at a guessed value [10] of 48 k€/m^3, or up to 230 k€/ton for raw graphite waste.

In England and Wales, the cost for a similar route is projected by NDA at about 5.3 k€/ton [11]. The huge difference between the former and latter numbers can be assigned to diverging assessments both in unit volume costs (ANDRA revised its own up by a factor 2.3 in 2009) and in density (assuming

1.25 ton of graphite per m^3 in the UK vs 0.24 ton/m^3 in France). Some future convergence of projected costs over the Channel's opposite shores is likely.

7. CONCLUSION

The injection of irradiated graphite waste in deep, depleted hydrocarbon reservoirs, although presently but a concept, hints at a large cost advantage over the default solution (in France) or reference solution (in England and Wales) for ILW. It has against it not to be reversible and its eschewing neat packages may for a time distract engineers trained in nuclear waste management.

As a burial solution for graphite waste, though, it is highly practical, re-using existing extraction sites and drawing on standard industrial practice. And, although research must be done to warrant the statement, in all likelihood its long-term health impact won't come close, by fair margins, to those of surface and shallow repositories.

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