NUCLEAR HYDROGEN PRODUCTION: SCOPING THE SAFETY ISSUES

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Abstract

Nuclear Hydrogen Production (NHP), a proposed scheme for producing hydrogen from non-fossil sources, uses high-temperature nuclear heat for thermo-chemical hydrolysis. There is also an electrochemical variant, where nuclear heat is used to generate steam, which is then electrolyzed to yield both oxygen and hydrogen. The thermo-chemical schemes need high temperatures, above 900 C, for efficient hydrogen production, and this focuses attention on coolants capable of supplying heat at high temperatures, such as gaseous helium, liquid salts and supercritical water. The possibility of using such coolants has been studied within different (fission) reactor concepts: for example, the helium-cooled Very High Temperature Reactor (the standard high-temperature reactor variant, known simply as VHTR), the liquid salt cooled very high temperature reactor (LS-VHTR) and the supercritical water cooled reactor (SCWR) respectively. In addition, *fusion* reactor concepts also using helium, liquid salts or supercritical water as coolants have been studied as sources of heat for nuclear hydrogen production (both magnetic fusion and laser fusion reactors have been studied for this purpose). Nuclear hydrogen production, in any of these versions, is a novel nuclear application, and this paper is devoted to a broad scoping analysis of its safety issues, as a contribution to regulatory and technological foresight. Possible applications of this and related technologies in tar sand processing are also discussed.

1.   Introduction

Much interest has recently been evinced in the possibility that nuclear-generated heat, electricity or steam might be used in hydrogen production, especially in the context of a future hydrogen economy, and as an attempt to reduce the greenhouse intensity of current means of processing and refining heavy hydrocarbons. A significant R&D effort is being undertaken to develop the enabling technologies for nuclear hydrogen production, both in Canada and in other countries. Nuclear Hydrogen Production, or NHP, is likely, in this scenario, to have a role both in the medium term (where the hydrogen produced will be used to upgrade and refine hydrocarbons), as well as in the long-term where it is envisaged that it will supply hydrogen for the hydrogen-fuelled transportation

that might come to exist. In either case, nuclear hydrogen production will have a smaller carbon emissions footprint than alternative methods of hydrogen production that are in use today.

Most of the new demand for hydrogen in Canada - which the Canadian Hydrogen Association estimates is likely to triple between now and 2020 - is forecast to arise from the hydrogen utilization that is anticipated in hydrogenating the lower-grade heavy hydrocarbons (mainly bitumen) in the tar sands for conversion to higher grade 'sweeter' hydrocarbons. Hydrogen will be need both in the pre-refining stage processing as well as during refining itself. Hydrogen is also forecast to be used in related applications such as coal liquefaction and synthetic fuel production – where, depending on the method used, it can also be generated as a side-product.

At the present time, hydrogen required in heavy hydrocarbon processing is produced by a method known as methane steam reforming. Here the feedstock hydrocarbon is mainly natural gas (though other hydrocarbons are also less commonly used as feedstock). Natural gas is also used in the reforming process as fuel in generating steam, which is the other feedstock in the process. This method of hydrogen production thus generates carbon dioxide in both steps of the process – in generating steam as well as in reforming methane.

In the case of bitumen from the tar sands, mere extraction also requires heat – in order that the bitumen may flow more easily – so that it may be pumped out for further processing. This method is known as *in situ* tar liquefaction, since the tar (bitumen) is liquefied on site. The heat needed is currently supplied through steam pumped into the tar sands directly (a process known as Steam Assisted Gravity Drainage, SAGD). The heat required for making this steam today is also obtained from hydrocarbon combustion.

Thus one notes that the heat, the steam and the hydrogen that is needed in tar sand processing are currently generated via processes that emit greenhouse gases. Nuclear technologies can potentially supply both the heat (either as steam or with other heat transfer fluids) and the hydrogen (produced using steam) that is required in tar sand processing – without emitting greenhouse gases. An intriguing suggestion recently made uses piped liquid salts as heat transfer fluids in place of steam. Liquid salts, of course, have been previously studied as coolants for nuclear reactors, where they commend themselves with their high boiling points, high specific heats and low viscosities. The

proposal is that such liquid salts could transfer nuclear heat from reactors to the tar sands in vertical piped loops through the tar sand wells. This would melt the tar, so that it may be more easily pumped and extracted. In the overall technology, liquid salts could thus appear in an interesting triple role: (i) as primary nuclear coolants for generating steam in power production (ii) as secondary heat transfer fluids to a thermo-chemical process for hydrogen production and (iii) as tertiary heat transfer fluids for tar liquefaction.

While the possible use of nuclear technology in tar sand processing is thus being actively explored, the determination of which combination of these options is most suitable has not yet been arrived at. However, in many of the technology variants being considered, chemical or hydrocarbon processing plants are likely to come to be co-located with nuclear plants. Since this is unprecedented, a scoping safety analysis becomes necessary in undertaking technology and regulatory foresighting of the process.

The rest of this paper is structured as follows. In **Section 2**, I discuss nuclear thermo-chemical hydrolysis as well as nuclear electrolysis for hydrogen production. In **Section 3**, safety issues in Nuclear Hydrogen Production are discussed, while in **Section 4**, I discuss designs to mitigate some of these risks. **Section 5** concludes.

2.   Nuclear Hydrogen Production

Hydrogen, the most abundant element in the universe, is not found on earth in its elemental form, because it reacts easily, forming hydrides, hydrates, hydrocarbons and carbohydrates. The most common means of producing hydrogen today is by separating it from hydrocarbons – but these processes involve the emission of greenhouse gases, primarily carbon dioxide. Water, on the other hand, is an easily available form of hydrogen. Splitting the water molecule produces only oxygen as a direct by-product. Therefore, the effort to develop greenhouse-emission free hydrogen production technologies has mainly focused on splitting water, hydrolysis. Since water is a stably bound molecule at ordinary temperatures, it costs energy to split the water molecule. The advantage of nuclear energy in this context is the fact that the technology is versatile and quite mature; the fact that high temperatures needed for hydrolysis can be reached safely, and that the heat required can be transported easily.

2 a. Thermochemical Hydrolysis

Thermochemical hydrolysis works by trapping the hydrogen from water in a compound such as hydrogen iodide (HI) from which it can then be easily dissociated thermally. The hydrogen yield comes from his thermal dissociation reaction. Several dozen such cycles have been studied; most current effort centers on two of these: the Sulphur Iodine (S-I) process where sulphuric acid is used to trap water reacting with sulphur dioxide, and hydrogen iodide, which serves as the source of easily dissociated hydrogen. See Figure 1 for details of the process. The other cycle of interest is the Copper-Chlorine (Cu-Cl) cycle where cuprous, cupric, and copper oxy-chloride are used, trapping the hydrogen from water in hydrochloric acid, from which it is then thermally dissociated.
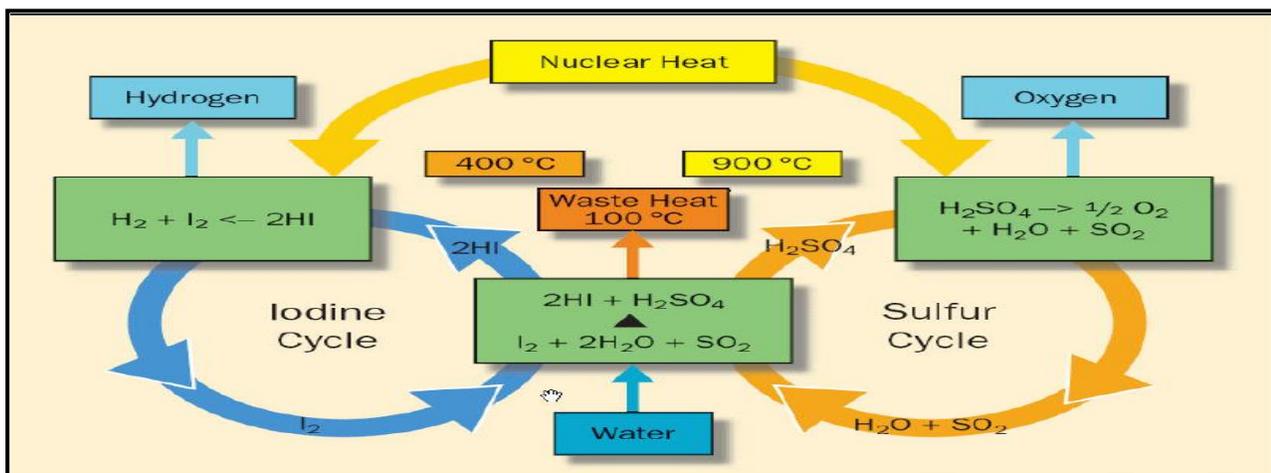
Figure 1: S-I cycle. The heat required is envisaged to come from a Very High Temperature Reactor (VHTR). The coolant in the VHTR will initially be helium.

2 b. High Temperature Electrolytic Hydrolysis (HTE)

High Temperature Electrolysis (HTE) process envisages feeding high temperature steam generated from nuclear heat into a special solid oxide fuel cell (SOFC) that is run in reverse mode (in the forward mode, the SOFC burns hydrogen to yield water).

Figure 2: High Temperature Electrolysis (HTE) scheme for Nuclear Hydrogen Production, showing the coupling to the nuclear plant. The nuclear reactor provides high temperature steam, and to the electrolysis cells it also provides electricity.

2 c. High Temperature Heat

Although the two hydrolysis schemes outlined above will work at lower temperatures, their efficiency exceeds 50% only when a temperature of 900 C is crossed. The efficiency of the S-I process is particularly strongly dependent on temperature.

Traditional water-cooled reactors, whether using pressurized or boiling water as coolants, have a maximum achievable outlet temperature of about 300 C. They cannot supply the heat necessary for either thermochemical or electrolytic hydrogen production to occur with acceptable efficiency. This upper limit in reactor outlet temperatures achievable with pressurized water reactors, or boiling water reactors is an inherent design constraint, and also limits their thermal efficiencies, and cannot be overcome within the design envelope of water cooled reactors.

Therefore, nuclear reactor designs which allow the coolant to achieve higher temperatures must be investigated – motivated both by the need to increase the reactor's basic thermal efficiency and the

need for hydrogen production at acceptable efficiency. Phase changes in water are the major complicating factor (also for any other low-boiling liquid coolants). The dual phase flow which occurs in consequence of phase changes within the operating range can have serious safety implications, and this must be carefully considered.

Gas coolants are free of this constraint, and may be safely heated to very high temperatures. However, if the gas is chemically reactive, this can be a serious issue; thus helium, an inert gas, is the preferred coolant for high temperature reactors. These considerations lead to the basic variant of the **VHTR** (Very High Temperature Reactor). Alternatively, a water cooled reactor may operate in the supercritical regime leading to the Supercritical Water-cooled Reactor concept, **SCWR** [2]. Here both high temperatures and high pressures are required.

A third option is to use liquid salts, like Flinak (which is a LiF-KF-NaF mixture in the ratio 46.5-11.5-42) that melts at the high temperature of 454 C and boils at 1570 C. Its heat capacity is about the same as that of water, 1 cal/g. A reactor concept developed with such a coolant has the acronym '**AHTR**' for Advanced High Temperature Reactor, also called **LS-VHTR,** for liquid salt-cooled very high temperature reactor.

The pressure-tube based CANDU-SCWR concept has been scoped at an outlet temperature of 625 C, while the pressure vessel version of the SCWR concept, RPV-SCWR is scoped at an outlet temperature of about 500 C. A CANDU-SCWR could thus provide steam at temperatures needed for the Cu-Cl cycle, while the VHTR, whether helium or liquid salt cooled, can supply heat at the temperatures required for the S-I cycle. Figure 4 shows the basic heat transfer loops in a future nuclear hydrogen production facility.
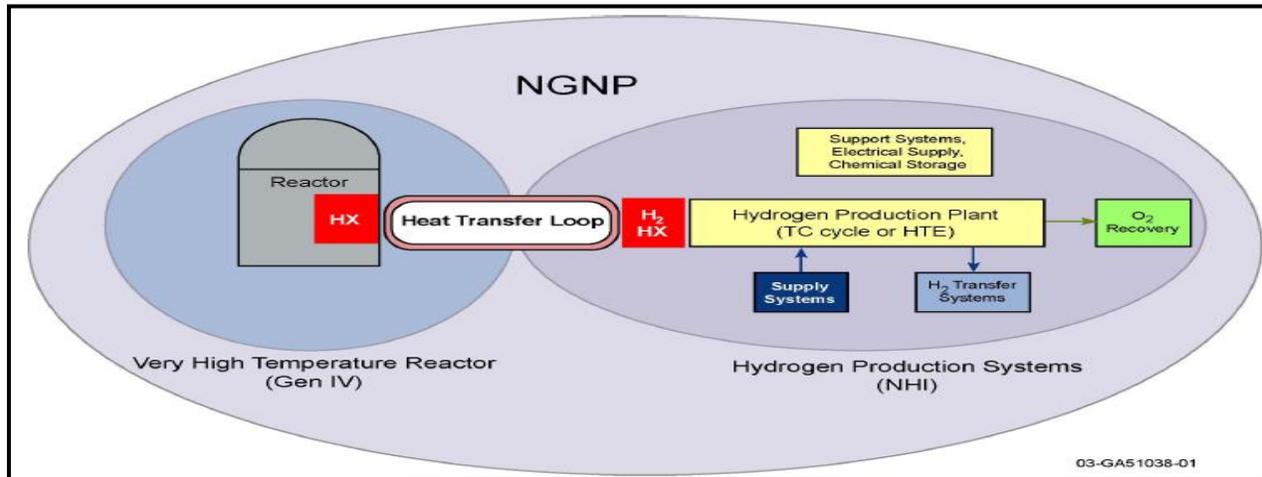
Figure 3: The basic layout of a nuclear hydrogen facility. (From Sherman 2006).

2 d. Heat Transfer Fluids

Heat transfer fluids are needed for *in situ* liquefaction of the bitumen in the tar sands. Currently, steam serves this need in the SAGD (Steam Assisted Gravity Drainage) process. However, liquid salts also have attractive properties that commend themselves for consideration. Forsberg (2007) proposes the scheme shown in Figure 5.

A nuclear reactor heats liquid salts that then circulate through vertical pipes in subsurface heat transfer loops in the tar sands. The liquefied bitumen/tar can then be pumped up to the surface through separate wells. The liquid salts can flow vertically down by gravity, and do not need to be pumped down like steam – although they will need to be pumped back up to keep the circulation going. It is contended that this process is more heat-efficient than the use of steam would be.
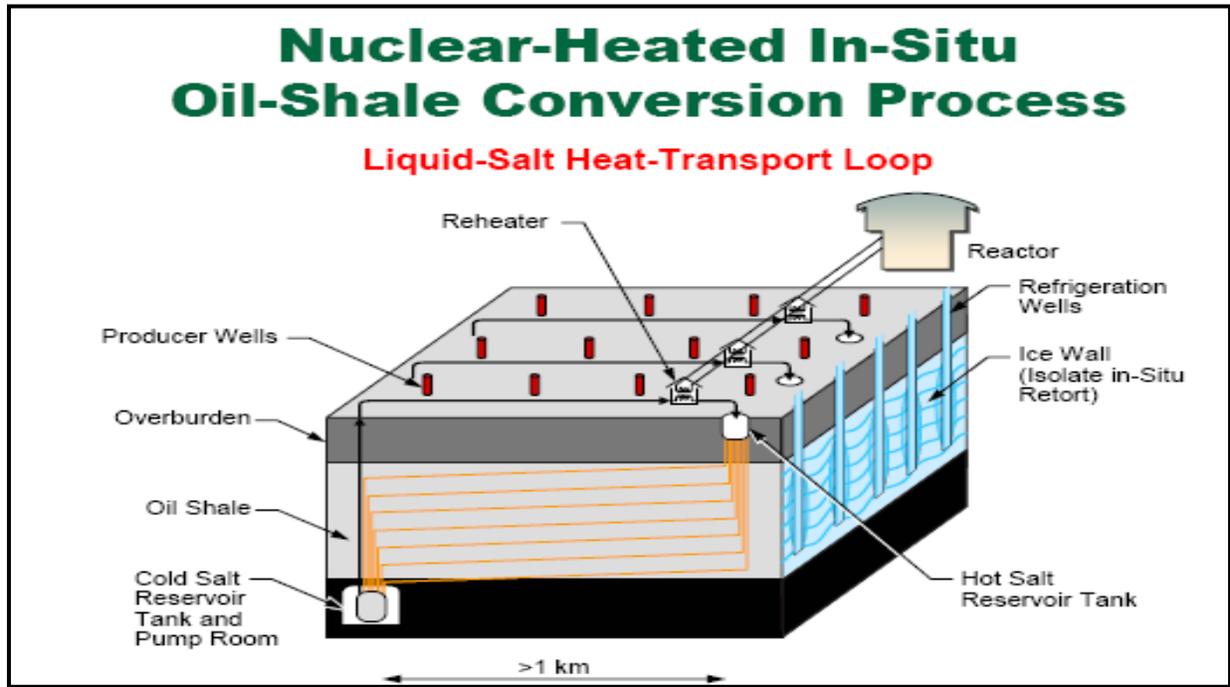
Figure 4: An *in situ* liquefaction process scheme that uses liquid salts as heat transfer fluids. (Forsberg 2007).

3. Scoping the Safety Issues in Nuclear Hydrogen Production (NHP)

Two conceptually separate parts of the nuclear hydrogen production facility may be distinguished – the nuclear reactor (which supplies heat and electricity, and for the nuclear methane reforming process, also steam), and the thermo-electrochemical or electrolysis plant(s) which produce(s) the hydrogen. Separate safety issues arise in each context separately, and significant amounts of analyses have been conducted in the past in considering the risks separately. For the nuclear plant, safety analyses have traditionally considered safety issues for the core, especially criticality control, and the safety of the thermal hydraulic loop, especially the possibility of loss of coolant through pipe ruptures.

Chemical safety analyses have focused on a number of possibilities including fires, leaks, spills and explosions resulting either from regular operating conditions in the plants, or excursions from the operating conditions. However, the increase in the risk profile of a plant from a combined nuclear-chemical location has not been considered in depth so far. Separate from other chemical plants, hydrogen plants are thought to be riskier from the intrinsic flammable nature of hydrogen, and this is significant also in the public perception of hydrogen. It can therefore be expected that concerns will be raised about the technology, and a comprehensive analysis of any new safety issues with this technology must be conducted. This is a first step scoping analysis in that direction.

At the reactor level, the SCWR is a concept that has not been previously constructed (although it *had* been scoped out in the 1950s, materials issues at the time were judged significant enough to deter construction, see Ref.1). Thus a comprehensive safety analysis of the SCWR will need to be done, quite separately of the interest in using it for nuclear hydrogen production. For the VHTR, both the helium-cooled and the liquid salt cooled variants *were* constructed in the past, and thus a body of operating and safety knowledge about them exists. Further analyses would, however, certainly be needed, and will be carried out as they move toward deployment.

As it happens, both uranium and thorium fuelled helium-cooled VHTRs *were* built in the past, although subsequently, all of them were shut down for poor operating performance. At this time, Japan and China are the only two nations that operate helium-cooled high-temperature **test**

reactors (HTTRs), and both are engaged in constructing full-fledged helium-cooled power reactors. Japan also operates a hydrogen production test facility that draws heat from a 30 MW helium-cooled test reactor, and is quite well advanced on the path to running it on a commercial scale. These reactors are now generating useful data on operational issues that will be important in future safety assessments for operational deployments.

While hydrogen *production* facilities have never been co-located with nuclear power plants before, the *use* of hydrogen in nuclear facilities is a routine operational matter. Hydrogen is used in BWRs and PWRs to control the pH of light water coolants. Hydrogen and nuclear technologies are therefore, in this sense, hardly strangers. Hydrogen is stored on LWR site locations, and is pumped directly into coolant loops whenever pH control requires it. Safety codes therefore already do exist that govern the how much, where, and how close hydrogen may be stored near a nuclear reactor. These codes governing quantity, location and proximity are motivated primarily by the need to prevent damage to the nuclear reactor core from hydrogen explosions and fires. The analysis that forms the basis of such safety codes and standards for stand-alone nuclear power facilities will likely also apply to future co-located hydrogen production facilities and nuclear plants.

As well, some of these codes are applicable irrespective of where the hydrogen is used or what it is used for – hydrogen being a flammable, volatile gas, a body of safety codes will apply to its storage and use in *any* context. The analysis underlying these generic hydrogen usage codes will also likely be generally applicable to nuclear hydrogen production facilities.

Qualitatively new safety issues in nuclear hydrogen production (NHP) will arise, however, from the following considerations.

(i) Proximate location of the Chemical Plant to a Nuclear Plant. The chemical plant will not only have hydrogen but also toxic chemical species, such as Sulphur dioxide for the S-I process and Hydrochloric Acid for the Cu-Cl process. Furthermore, these will be under high temperatures and pressures. These chemicals will tend to escape *physically* through leaks, and moreover, also tend to *chemically corrode* their piping and containment systems, and their leakage may also have toxic effects. The produced hydrogen, especially if stored, could also

leak, and leakage may lead to detonation or deflagration. This latter risk is reasonably well understood, but the overall risk needs to be analysed thoroughly.

(ii)   Differences in Safety Philosophies One point hear bears emphasis: the philosophy underlying chemical risk mitigation is in some ways at odds with the philosophy underlying nuclear risk mitigation. While dispersal and diffusion of chemicals, dilution with air and/or water, reduction of concentration by all means at hand, and thorough ventilation of enclosed spaces form the basis of chemical risk mitigation, in some ways the opposite is true of nuclear risks – where one speaks of containment, confinement, sequestration and isolation of nuclear materials; separation from water and circulating air; and prevention of diffusion and dispersal of radioactive species. These differences in overall governing philosophy will need to be carefully considered in the overall safety analysis of co-located nuclear-chemical plants. For radiochemical species, the two safety philosophies can converge, thus there is certainly scope for a proper balance between the two in implementation.

(iii)   Hydrogen Storage: Most of the risk from stored hydrogen arises from the flammability of hydrogen, which can deflagrate or detonate even just on leaking from a storage container. Based on the historical record of hydrogen detonation and deflagration events in LWR locations, Smith *et al* (2005) have published a study which quantifies the risk and extrapolates a minimum distance between chemical and nuclear plants, to keep the probability of nuclear core damage below the regulatory thresholds.

(iv)   Hydrogen Production in large quantities (as opposed to merely storage). The continuous local production of hydrogen will likely require that codes established for local hydrogen storage be modified, perhaps to require that the produced hydrogen be piped away so as to keep the actual stored hydrogen below a set threshold. As well, the nature of the pipes may have to be specified (for example, that they be double walled to reduce leaks and related detonation/deflagration possibilities). An additional consideration is that some of the produced hydrogen will be in the form of tritium, and, this is more especially the case for High Temperature Electrolysis, which has a significant tritium yield. However, if helium is used as a coolant in the nuclear reactor, there is also the possibility of a tritium yield through neutron activation of the He^3 isotope, which may diffuse through the heat exchanger to end

up in the produced hydrogen. Even in traditional PWR or PHWRs, tritium is generated in the coolant and moderator loops and the risk and yield is analysed and planned for.

(v)   <u>Heat Transfer Fluids</u>. Even in the simplest conception of the combined nuclear-thermo-electrochemical plant, there will be at least two additional thermo-hydraulic/gasdynamic loops. This increases the plant complexity and more comprehensive Loss of Coolant Analyses will need to be done.

(vi)   <u>The Use of Helium:</u> as a coolant in the power generating cycle, and also as a possible heat transfer fluid between nuclear plant and chemical plant. This could potentially lead to the product hydrogen becoming contaminated by tritium. This happens when the He^3 isotope absorbs a thermal neutron and emits a proton (H^1, regular hydrogen, protium) and H^3, tritium.

(vii)   <u>Helium is chemically inert</u>, but it can embrittle metals and alloys without chemical reactions, simply by diffusing into grain boundary locations. Extensive use of helium in plant thermalhydraulic and thermal-fluidic roles may have an effect on plant structural integrity, which must be considered.

(viii)   <u>Flinak</u> – the liquid salt proposed as a possible heat transfer fluid, has a lithium component with a non-negligible cross section for converting to tritium on neutron activation. (Ohashi 2007). In addition, Flinak and related salts have corrosive properties which must be balanced against their usefulness as heat transfer fluids. Thus both flinak and helium have the possibility of generating tritium and in separate ways can affect plant structural integrity. This must be carefully considered in comprehensive nuclear hydrogen plant safety analyses that are done for any future facility.

4. Design Modifications for Risk Mitigation

While a number of broad safety issues are scoped out above, a study of smaller scope that examined the additional risk arising from local storage of hydrogen to a nuclear plant was carried out by the Idaho National Laboratory in the US. This study also examined a number of risk mitigating design modifications and the effect these had on the overall quantitative core damage frequency measure. The traditional focus in a Probabilistic Safety Analysis of nuclear plants is the core damage frequency by *internal events* (such as loss of cooling). Here the core damage frequency from an **external event** (detonation impacts from stored hydrogen) was analysed. The Table below shows the results.

Case	Description	Mean Core Damage Frequency (per year)	Mean Chemical Dispersion Frequency (per year)
Nominal	No mitigating features and the separation is set at 60m	7.00E-06	3.00E-03
1	Varying the Distance between Nuclear and Hydrogen Production Facilities	See Note below	3.00E-03
2	Constructing an earthen barrier between the nuclear and chemical facilities	4.00E-10	3.00E-03
3	Constructing the Nuclear Facility primarily underground	4.00E-10	3.00E-03
4	Constructing Blast Panels near the Chemical Facility to dampen overpressure events	4.00E-10	3.00E-03
5	Constructing the Chemical Facility primarily underground	8.00E-11	8.00E-04
6	Moving the Nuclear Plant Control Room offsite	7.00E-06	Releases no longer impact control room

Table: Risk Mitigating Design Modifications: Impact on Base Case Safety Risk (adapted from Smith et al 2006). **Note**: The direct core damage risk decreases monotonically with distance to about 80m, but flattens out before declining further. Beyond 80 m, the indirect core damage occurring from hydrogen explosions that first damage other parts of the nuclear plant becomes a significant component of total risk. Both risks decline significantly beyond 100m.

The basic conclusion is that separation distances between the chemical plant and the nuclear reactor in the range of 60 m to 120 m are likely to be adequate to reduce core damage risk from hydrogen leaks that lead to explosions – to below 1E-9 (Smith *et al.*, 2005). This minimum distance has implications also for which heat transfer fluid is ultimately chosen to transfer heat between the nuclear reactor and the chemical plant, because gaseous and liquid coolants will require vastly different amounts of pumping power to transfer heat between such distances. If a liquid salt heat transfer fluid like Flinak is used, it can flow at low pumping pressure, which consumes less energy, while if a gaseous coolant like helium is used, much higher pressures will be required, consuming more energy.

The INL study is notable for having studied risk mitigating strategies such as constructing either the nuclear or the chemical plant underground. However, the study (Smith 2005) did not analyze separately the possible new risk arising from novel core designs, fueling modes or new coolants in the thermalhydraulic loops that are under consideration for the nuclear plant itself, because adressing those risks is a major component of the Generation IV Program anyway. Prior to licensing a nuclear hydrogen production plant, a combined PSA will be needed, so that the joint risk probability in the entire nuclear-thermochemical complex can be accurately understood.

The Idaho National Laboratory analyses also recommended that

  (i) A 100 kg on-site limit be imposed on hydrogen storage,

  (ii) That double-walled pipes be used for piping the produced hydrogen, which should be piped away as soon as it is produced (this reduces the chances of hydrogen leakage through rupture of any given pipe. Hydrogen can deflagrate or detonate simply on leaking from under pressure – the conditional probability of which the study carefully quantified),

  (iii) The nuclear plant control room should be located outside the dispersal zone for chemical releases, and the study also quantified the distance by considering the atmospheric diffusion 'footprint' from the gases such as sulfur dioxide or hydrogen halides that the chemical plant could release. This design modification does not change

core-damage risk from the debris that any possible hydrogen detonation could create, but it reduces the possibility of toxic gas exposure to negligible levels, and thus reduces to zero the probability of any core damage that could result from incapacitated control room personnel.

6. Conclusion

This paper has presented a broad scoping analysis of safety issues for Nuclear Hydrogen Production, and considered the broad design modifications that could mitigate some of the safety risks. In particular, the design modifications needed to mitigate the class of safety risks that arise from local storage of hydrogen produced by NHP have been summarized. The paper is a contribution to technology and regulatory foresighting, and is intended to stimulate further analytical work, and to signal the need for a careful safety analysis of the entire nuclear hydrogen production process, which is a prototype for non-power process heat applications of nuclear energy.

Citation: Baindur, S. *Nuclear Hydrogen Production: Scoping the Safety Issues,* Canadian Nuclear Society Ottawa, January 24 2008

References

[1] Baindur, S., "Materials Challenges for the Supercritical Water-cooled Reactor (SCWR)", Proceedings of the *Canadian Nuclear Society Annual Conference,* Saint John, New Brunswick, June 3-6, 2007.

[2] Baindur, S. "Nuclear Hydrogen Production: Re-examining the Fusion Option", Proceedings of the *Canadian Hydrogen Association Workshop on Non-fossil Hydrogen Production*, Oshawa Ontario, 30 May 2007.

[3] Baindur, S. "Safety Issues in Nuclear Hydrogen Production with the Very High Temperature Reactor (VHTR)", to appear, Annual Conference of the Canadian Nuclear Society 2008, Toronto.

[4] Davis, C.B., Barner, R.B., Sherman, S.R. and Wilson, D.F., "Thermal-Hydraulic Analyses of Heat Transfer Fluid Requirements and Characteristics for Coupling a Hydrogen Product Plant to a High-Temperature Nuclear Reactor", Idaho National Laboratory Report, *INL/EXT-05-00453*, 2005.

[5] Forsberg, C., "Assessment of Nuclear-Hydrogen Synergies with Renewable Energy Systems and Coal Liquefaction Processes", Oak Ridge Laboratory Report, *ORNL/TM-2006/114*.

[6] IAEA, "Hydrogen as an Energy Carrier and its Production by Nuclear Power" TecDoc-1085, 1999

[7] Ohashi, H., and Sherman, S.R., "Tritium Accumulation and Movement in the NGNP System Interface and Hydrogen Plant", *INL-EXT-07-12746,* 2007.

[8] Smith, C., Beck, S. and Galyean, W., "Separation Requirements for a Hydrogen Production Plant and High Temperature Nuclear Reactor", *INL-EXT-05-00137*, October 2005.

[9] Verfondern, K. and Nishihara, T., "Valuation of the Safety Complex of the Combined Nuclear-Chemical Complex for the HTTR" Julich-4135, 2004.

[10] Yildiz, B., Petri, M., Conzelmann, G., and Forsberg, C., "Configuration and Technology Implications of Potential Nuclear Hydrogen System Applications", Argonne National Laboratory Report ANL-05/30, 2005.