Use of Dissociating Gases as Primary Coolants and Working Fluids in Power Cycles for Fusion Reactors

M. Z. Hasan, R. C. Martin
University of California, Los Angeles, CA USA

ABSTRACT

The prospect of employing dissociating gases as primary coolants for removing the thermal power from a fusion reactor core and as working fluids in power cycles for converting this thermal power to electricity is investigated. Chemically reacting gases which undergo endothermic dissociation reaction when heated and exothermic recombination reaction when cooled, generally exhibit superior heat transfer performance as heat transfer media and their thermodynamic properties result in an improved power cycle performance. Existing literatures are surveyed to identify prospective dissociating gases for fusion applications. The performance of these gases with respect to the specific environment and requirements of fusion reactors are evaluated.

INTRODUCTION

The attractiveness of fusion power reactors depends to a great extent upon safe and economic engineering design of the reactor core and efficient conversion of the recovered thermal energy to electricity. The primary coolant plays an important role in removing the thermal power from the first wall, blanket and limiter/divertor plates of a fusion reactor. Among the desirable properties of a primary coolant are high heat transfer coefficient, low system pressure, low circulation power, suitably large temperature range of operation, compatibility with structural material, and favorable neutronic and safety properties. There is no single coolant, liquid or gaseous, which has the best of every desirable property.

At present Rankine cycle and Brayton cycle are used for power conversion in fossil-fuel and nuclear fission power plants. The working fluid for Rankine cycle is steam and that for Brayton cycle is an inert gas such as helium. Two limitations of steam are relatively low maximum cycle temperature and large specific volume at the required low condenser pressure which requires multiple exhausts and large and/or several low-pressure turbines. The main drawback of a Brayton cycle using an inert gas as working fluid is the large compressor power which reduces efficiency.

The search for ideal primary coolant and working fluid for power cycle is a continuous one. Many fluids have been proposed for fusion reactor primary coolant. Among them are water, liquid metals, aqueous salt solution, molten salt and inert gases. One version of the on-going ARIES tokamak fusion reactor study (Najmabadi, 1988) has proposed the use of a gas coolant with suspended solid particulates as the primary coolant (Wong and Hasan, 1989).

Theoretical and experimental studies have been undertaken to investigate the performance of certain chemically reacting gases as heat transfer media and working fluids for both Brayton and Rankine cycles. A partial list of these reacting gases together with a few of the relevant properties is given in Table 1. Nitrogen tetroxide (N_2O_4) and nitrosyl chloride ($NOCl$), have drawn most of the attention from the researchers. Physical properties of these two gases are given in Table 2. Recent studies in the Soviet Union emphasize their use as primary coolants and working fluids in power cycle for fission power plants.

Table 1: A partial list of dissociating gases*			
Dissociating gas	$C^{\dagger}$	$\Delta H_r^{\star}$	T-Range(^oC)
$N_2O_4 \rightleftharpoons 2NO_2$	2	13.7	25-170
$2NO_2 \rightleftharpoons 2NO + O_2$	1.5	27.0	140-850
$2NOCl \rightleftharpoons 2NO + Cl_2$	1.5	9.21	25-900
$Al_2Br_6 \rightleftharpoons 2AlBr_3$	2	30.0	300-1400
$Al_2Cl_6 \rightleftharpoons 2AlCl_3$	2	29.8	200-1100
$Al_2Br_6 + 4Al(liq) \rightleftharpoons 6AlBr$	6	282.4	670-1400
$Al_2Cl_6 + 4Al(liq) \rightleftharpoons 6AlCl$	6	263.8	670-1200

* Nesterenko (1975).

† Coeff. of increase of gas constant.

⋆ Heat of reaction, $Kcal/g.mole$.

Table 2: Properties of N_2O_4 and $NOCl$.*		
Property	N_2O_4	$NOCl$
Mol. wt. (g/mole)	92.02	65.46
Boiling pt.(^oC)	21.3	-5.8
Melting. pt. (^oC)	-11	-61.5
Crit. temp. (^oC)	158.3	167.5
Crit. pres. (atm)	103.3	90.0
ΔH_r ($Kcal/Kg$)	149/293	141.7
Reaction	$N_2O_4 \rightleftharpoons$ $2NO_2 \rightleftharpoons$ $2NO + O_2$	$2NOCl \rightleftharpoons$ $2NO + Cl_2$
Temp. Range(^oC):		
1 atm	25-850	25-900
100 atm	25-1200	—

* Nesterenko (1975) and Huang (1986).

The objectives of this paper are to evaluate the use of these chemically reacting gases as primary coolants and power-cycle working fluids for fusion reactor applications, and to review previous works in this area.

DISSOCIATING GASES AS HEAT TRANSFER MEDIA

Previous experimental and theoretical studies have found an increase in heat transfer coefficient, h, for dissociating gases compared to non-reacting gases within the temperature range of dissociation reaction. For a dissociating gas, the effective specific heat capacity, Cp_{eff}, increases due to the absorption of heat during dissociation (endothermic reaction). The effective thermal conductivity, k_{eff}, increases due to increased molecular diffusion driven by the concentration gradients within the reacting system.

Irving and Smith (1961) performed theoretical analysis of turbulent-flow heat transfer of the N_2O_4 reacting system using effective thermal conductivity and specific heat capacity, and adapting Reynolds, Colburn and Deissler analogies in the temperature range 300 to 370^oK and Reynolds number (Re) range 10^4 to 2×10^5. They calculated a maximum increase of about 10 times in h over that for a non-reacting system. The magnitude of heat transfer coefficient depends on the temperature of the gas, i.e. the degree of completion of the dissociation reaction. Krieve and Mason (1961) experimentally measured h in turbulent pipe flow of N_2O_4 for Re 6.7×10^3 to 2.2×10^4 and gas temperature 295 to 361^oK. The maximum increase of average value of h measured was 14 times. Their proposed correlation for Nusselt number (Nu) is

$$Nu = 0.018 Re^{0.8} Pr^{1/3}, \tag{1}$$

where Pr is Prandtl number. The gas properties are evaluated at the average gas temperature. Experimental work done in the Soviet Union (Devoyno, 1975) for N_2O_4 up to $p = 60\ atm$, $Re \leq 3 \times 10^5$, and $T \leq 550^oC$ suggests the following correlation for Nusselt number:

$$Nu = 0.021 Re^{0.8} Pr^{0.43} (\frac{T_w}{T_f}), \tag{2}$$

where T_w and T_f are wall and gas temperatures, respectively. Devoyno et al. (1973) have correlated experimental data for Nu during cooling of N_2O_4 system by the following expression.

$$Nu = 0.021 Re^{0.8} Pr^{0.43} (1.27 - 0.27\frac{T_w}{T_f}). \tag{3}$$

The ranges of parameters were: $p = 5.5\ to\ 80\ atm$, $Re = 1.25 \times 10^4\ to\ 1.0 \times 10^5$, and the inlet temperature of the gas, $T_f \leq 800^oK$. The heat transfer coefficient measured was 1.5 to 6 times higher than that of a "frozen" gas.

To evaluate N_2O_4 as a heat-transfer medium, we compare its performance with that of helium for cooling a hypothetical system. For a tube 1 m long with 1 cm inner diameter and a uniform surface heat flux of 0.5 MW/m^2, the inlet and outlet temperatures for both coolants are assumed to be 300 and 1000 ^oK, respectively. The density(ρ), specific heat capacity (Cp), thermal conductivity (k), and kinematic viscosity (μ) of N_2O_4 system (equilibrium mixture of N_2O_4, NO_2, NO, and O_2) are derived from the data of Fan and Mason (1962) and shown in Figure 1. The pressure is one atmosphere. The calculated velocity of N_2O_4 system at inlet is 37.8 m/s and at exit is 308.7 m/s. At atmospheric pressure, the required velocity for He is very large. Therefore, a pressure of 10 atm is assumed for He. The velocities of He at the inlet and exit of the tube are 47.4 m/s and 158 m/s, respectively. Figure 2 shows the heat transfer coefficients of the dissociating gas and helium as functions of temperature. Equation (1) is used to calculate the Nusselt number for N_2O_4 system. For He the same equation is used but with the leading coefficient of 0.023 instead of 0.018. At the inlet (300^oK) of the tube the heat transfer coefficient for N_2O_4 system is about 8 times larger than that for He. At the exit (1000^oK), the heat transfer coefficient of N_2O_4 system is about twice that of He.

Fig.1: Properties of N_2O_4 syst (at atmospheric pressure)

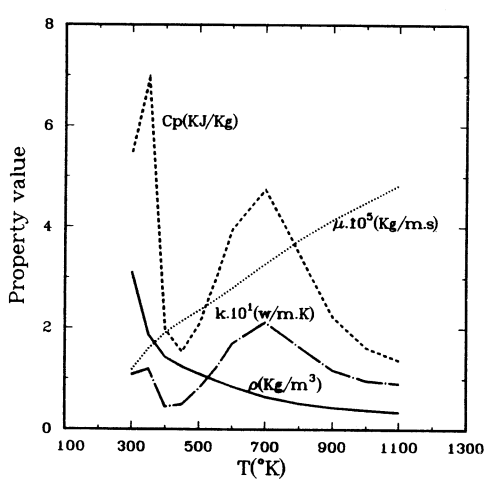
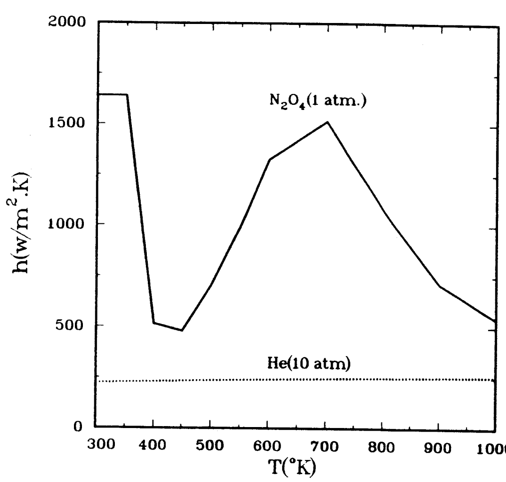


Fig. 2: h for He and N_2O_4 (d_i=1cm, L=1m, q"=0.5MW/m^2)



Physical and chemical properties of $NOCl$ have been reported by Marcus & Wohler (1961). Although no heat transfer experiment with $NOCl$ has been performed, Huang (1986) used equation (1) to calculate heat transfer coefficient for $NOCl$ employing effective values of thermal conductivity and specific heat capacity. This calculation predicted about a ten-fold increase in heat transfer coefficient for $NOCl$ compared with a non-dissociating gas.

Therefore, a dissociating gas generally is a better heat-transfer medium than an inert gas. A dissociating gas requires lower pressure and gives higher heat transfer coefficient compared with an inert gas such as He and CO_2. However, the increase in heat transfer coefficient is much smaller at high temperature where dissociation reaction runs to completion.

DISSOCIATING GAS AS WORKING FLUID IN POWER CYCLE

Fairly detailed studies of Brayton and Rankine cycle performances using dissociating gases as working fluids have been done. Kesavan and Osterle (1981) did a detailed study on the relative performances of $NOCl$ and He in a Brayton cycle. Huang and Govind (1988) have studied the performance of compound cycles using $NOCl$ or N_2O_4 in the topping Brayton cycle and N_2O_4 in the bottoming Rankine cycle. Nesterenko (1975) did a comparative study of the performances of various cycles using dissociating gases, inert gas, H_2O, and liquid-metals as working fluids. Sorokin (1979) has presented detailed thermodynamic properties of N_2O_4 system such as degree of dissociation, specific heat capacity, $T-S$ diagram, and $h-S$ or Mollier diagram, and has also studied the performance of cycles using N_2O_4 as working fluid and with or without the effect of reaction kinetics.

These studies show that the dissociating gases provide higher cycle efficiency compared to He and CO_2. Due to the decrease in the number of moles in the compressor (recombination at low temperature), the compression work is much less with dissociating gases. Regeneration is also more efficient due to the heat of reaction and better heat transfer for dissociating gases. With the smaller specific volume of the dissociating gases at low temperature, the low pressure turbine is smaller and has fewer stages compared to turbines for steam or inert gases. This reduces the length, weight, and cost of dissociating-gas turbines. Lomashev and Nesterenko (1975) reported a reduction of 3 to 5 times in weight and cost for turbines using N_2O_4, Al_2Cl_6, and Al_2Br_6 as working fluids compared with steam turbines. Table 3 gives thermal efficiencies of a few dissociating-gas cycles. Comparison of turbines using N_2O_4 and H_2O is given in table 4.

CHEMICAL AND RADIOLOGICAL PROPERTIES OF N_2O_4 AND $NOCL$

More information is available for N_2O_4 as a nuclear coolant than for $NOCl$ due to the ongoing research in the Soviet Union. The presence of NO_2 in the N_2O_4 system can cause toxicity, with prolonged exposure to ≥ 5 *ppm* NO_2 considered unsafe. Higher exposures cause respiratory and central nervous system problems, with concentrations ≥ 100 *ppm* being potentially fatal. Adequate ventilation and prevention of leaks is required near working areas. Toxicity concerns for the general public are not a major concern, with rapid dilution of any release to the environment.

Neutron activation of a N-based coolant produces radioactive ^{14}C from (n,p), (n,np), and (n,d) reactions, with the $^{14}N(n,p)^{14}C$ reaction being dominant. Creation of ^{14}C from

Table 3: Typical cycle efficiency

Cycle	$T_{max}(^{\circ}K)$	Eff.(%)
$NOCl-N_2O_4$	1000	55*
$N_2O_4-N_2O_4$	1000	51*
$AlBr_3-N_2O_4$	1000	48*
$Al_2Br_6-N_2O_4$	1000	56†
$NOCl$	900	40⋆

* Huang and Govind (1988).

† Nesterenko (1975).

⋆ Kesavan and Osterle (1981).

Table 4: N_2O_4 and H_2O turbines*

Item	N_2O_4	H_2O
Turbine output, MW	500	500
Pres. at turb. inlet (atm)	240	240
Temp. at turb. inlet ($^{\circ}C$)	565	580
Pres. at turb. exit (atm)	1.4	0.035
Number of stages	10	42
Length of turbine (m)	16.8	29.1
Weight of turbine ($tons$)	180	964
Cost, 1000 rubles	619	1600

* Lomashev and Nesterenko (1975).

^{15}N is only significant for neutrons with energies above 8 MeV. In a thermal neutron environment, a N_2O_4 coolant based on isotopically enriched ^{15}N could reduce ^{14}C production significantly, but in a 14 MeV neutron environment significant production of ^{14}C is unavoidable. A N_2O_4 coolant based on ^{15}N might reduce ^{14}C production by perhaps a factor of 10 in a fusion environment (Cheng, 1988), but would require the added expense and complexity of isotopic enrichment. The radiobiological hazard of ^{14}C is comparable to that of tritium in fusion reactors. The maximum permissible concentration (MPC) for the general public of ^{14}C in air is half that of tritium, while the MPC of ^{14}C in water is 20% that of tritium. A concern for waste disposal of ^{14}C is its long half-life (5730 years) compared to 12.3 years for tritium. For fusion reactor systems with a secondary coolant loop outside the fusion power core, the advantages of a dissociating gas coolant remain relevant without the activation concerns.

The reactivity of N_2O_4 with structural materials and impurities is enhanced by the presence of NO_2. Any water in the system can readily react with N_2O_4 to form nitric acid. NO_2 is extremely corrosive when wet, but NO_2 with less than 0.1% water can be safely stored in steel cylinders. Chromium-nickel steel has shown good stability to N_2O_4 corrosion from 200 to 700^oC (Kamenev, 1982). These reactive nitrogen oxides can cause fire if exposed to readily combustible chemicals or reactive organic materials, so common sense must be used in the choice of surrounding reactor materials.

A coolant called nitrine, based on N_2O_4 and containing extra nitric oxide (NO), has been under study in the Soviet Union (Nesterenko, 1982). The additional NO reduces corrosion and improves the kinetics of the recombination reactions. Studies on the stability of various insulators, sealing materials and lubricants in N_2O_4 have also been done. Some inorganic glass and enamel coatings for protection of stainless steel from N_2O_4 have been tested, with the enamel coating showing the best stability (Bakalin, 1985).

If used in the primary coolant loop, the chlorine in a $NOCl$-based coolant poses an activation hazard. The corrosiveness of $NOCl$ requires resistant alloys. An iron alloy containing 2.4% silicon and 32% chromium has good resistance. Nickel and nickel alloys containing silicon, molybdenum, chromium, copper, or iron also resist corrosion (Mellor, 1967).

APPLICATION TO FUSION REACTORS/CONCLUSIONS

The reversibility and stability of N_2O_4 as a heat-transfer medium and working fluid for power cycle has been demonstrated by prolonged use in a fast fission test reactor in the Soviet Union (Nesterenko, 1982). As heat transfer media, the dissociating gases are generally superior to inert gases. Compared with inert gases, they have higher heat-transfer coefficient especially at low temperatures, and require lower static pressure. Due to their high heat capacity and enhanced natural circulation from concentration gradient, the dissociating gases will improve safety margin during loss-of-flow accidents.

For such high-heat-flux components of a fusion reactor as the first wall and limiter/divertor plates, dissociating gases operating at relatively low temperature will perform much better than the inert-gas coolants. The blanket and shield have small heat load. Both inert-gas and dissociating-gas coolants will perform equally well for the blanket and shield.

Since dissociating gases provide higher power-cycle efficiency and require smaller turbine, regenerator and compressor units, a significant simplification in the design of the fusion reactor core and in the balance of plant can potentially be realized by using a suitable dissociating gas both as the primary coolant and working fluid for power cycle.

From the many candidate dissociating gases, N_2O_4 and $NOCl$ have received the most attention—the former as both coolant and working fluid for power cycle and the latter mainly as working fluid for power cycle. Since both of these gases are toxic, extra safety measures need to be taken. Activation of nitrogen and chlorine by fusion neutrons poses a radiological hazard. A detailed analysis of this hazard resulting from the use as primary coolants is required. In the areas of structural material selection and heat-transfer evaluation over much larger ranges of temperature, pressure and Reynolds number, further investigation is necessary, especially for $NOCl$.

REFERENCE

Bakalin, Yu.I. (1985). The Behavior of Glass and Enamel Coatings for Protection of Stainless Steel in Heated N2O4. Vestsi Akad. Navuk BSSR, Ser. Fiz.-Energ. Navuk, (4) 37-39.

Cheng, E.T. (1988). General Atomics, personal communication.

Devoyno, A.N. (1975). Experimental Study of Convective Heat Transfer in the Dissociating Gases. Published in Dissociating Gases as Heat-transfer Media and Working Fluids in Power Installations. ed. Krasin, A.K., American Pub. Co., New Delhi, p-199.

Devoyno, A.N., et al. (1973). Study of Convective Heat Transfer in Chemically Reacting Nitrogen Tetroxide. Heat Transfer, Soviet research, vol.5, No.5, p-83.

Fan, S.S.T. and Mason, D.M. (1962). Properties of the System $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$. J. Chem. and Engg. Data, vol.7, No.2, p-183.

Huang, H. (1986). Studies on Dissociating Gas Power Cycle. Ph.D. Dissertation, Univ. Cincinnati, Cincinnati, OH, p-60.

Huang, H. and Govind, R. (1988). Studies on Power Plants Using Dissociating Gases as Working Fluids. Chem. Eng. Comm., vol.72, p-95.

Irving, J.P. and Smith, J.M. (1961). Heat Transfer in a Chemically Reacting System (Nitrogen Tetroxide-Dioxide). AIChE Journal, vol.7, No.1, p-91.

Kamenev, A.Ya. (1982). Corrosion Behavior of Chromium-Nickel Steels in a Nitrogen Tetroxide Medium under Experimental Test Stand Operating Conditions. Vestsi Akad. Navuk BSSR, Ser. Fiz.-Energ. Navuk, (1) 41-44.

Kesavan, K. and Osterle, J.F. (1981). Brayton Cycle Using Dissociating Nitrosyl Chloride. Proc. 16th Intersoc. Energy Conv. Eng. Conf, p-2204.

Krieve, W.F. and Mason, D.M. (1961). Heat Transfer in Reacting Systems: Heat Transfer to Nitrogen Dioxide Gas Under Turbulent Pipe Flow Conditions. AIChE Journal, vol.7, No.2, p-277.

Lomashev, B.I. and Nesterenko, V.B. (1975). Gas Turbines with Dissociating Working Fluids," published in "Dissociating Gases as Heat-Transfer Media and Working Fluids in Power Installations. American Pub. Co., New Delhi, p-74.

Marcus, R.J. and Wohler, H.C. (1961). Photochemical Systems for Solar Energy Conversion: Nitrosyl Chloride. Solar Energy, vol.5, No.2, p-44.

Mellor's (1967). Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 8, Supp. 2, Longmans, Green and Co., London, p. 430.

Najmabadi, F. (1988). The ARIES Tokamak Fusion Reactor Study— The Scoping Phase. Proceedings of the 8th Topical Meeting on the Technology of Fusion Energy, Salt Lake City.

Nesterenko, V.B. (1982). Influence of the Thermal Effects of Chemical Reactions in a Dissociating Coolant on the Thermodynamic Efficiency of an Atomic Power Station. Soviet Atomic Energy, 52(1) 34-42.

Nesterenko, V. B. (1975). Thermodynamic Schemes and Cycles of APS Using the Dissociating Gases, published in Dissociating Gases as Heat-Transfer Media and Working Fluids in Power Installations. American Pub. Co., New Delhi, p-8.

Sorokin, A. (1979). Dissociating Nitrogen Tetroxide (N_2O_4) as a Working Fluid in Thermodynamic Cycle. Nuclear Science and Eng., vol.72, p-230.

Wong, C.C.P. and Hasan, M.Z. (1989). Thermal-Hydraulic Design of a Solid-Particulate Fusion Reactor Blanket. These proceedings.