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Control of Explosive Mixtures in PWR Waste Gas Systems

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Prepared for
U.S. Nuclear Regulatory
Commission

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ABSTRACT

A study has been performed to evaluate problems associated with the existence of flammable or explosive gas mixtures in Pressurized Water Reactor waste gas systems. Information on existing waste gas systems, waste gas concentrations, and gas monitoring instrumentation obtained from six operating nuclear power plants is summarized. A comparative risk evaluation has been performed for several generic types and configurations of PWR waste gas systems. Waste gas systems in the plants visited are included and categorized as part of the risk evaluation.

Existing data on the effect of initial pressure on flammability limits, as well as recently reported data on flammability and detonability of hydrogen/air mixtures has been collected and summarized. A survey of commercially available instruments for monitoring hydrogen and oxygen concentrations has been performed and the results tabulated. A series of observations, conclusions and recommendations are given.

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1. INTRODUCTION

All radioactive effluents from nuclear power plants are under the regulatory constraints given in 10 CFR 50, Appendix I. The objective of this regulation is the achievement of "As Low As Reasonably Achievable" (ALARA) exposures to the offsite public, as well as to plant personnel. Among the gaseous effluents normally emitted from nuclear power plants are the radioactive noble gases and halogens that result from fission of tramp uranium and from fuel cladding leaks. In order to control the quantity and rate of gases that are released to the environment, all nuclear power plants provide some form of holdup or storage. This allows the shorter-lived radioactive gases to decay to radiation levels that allow discharge while not exceeding compliance values. In most Boiling Water Reactors (BWRs), this decay is accomplished by a continuously flowing, once-through, off-gas treatment system that provides for adsorption and holdup of these gases in large charcoal beds. For Pressurized Water Reactors (PWRs), the commonly used approach is to collect the gases and store them in waste gas decay tanks. The contents are subsequently released to the environment at controlled rates after typical storage times of 30 to 45 days. In addition to these gases, all light-water reactors also produce hydrogen and oxygen due to radiolysis of primary coolant. These gases accompany the radioactive gases wherever primary coolant is degased. In PWRs, hydrogen is also added to the primary coolant system to scavenge oxygen for corrosion control, further contributing to the hydrogen source term in the gas collection system. Thus, in both PWRs and BWRs, there exists the potential for explosive mixtures of hydrogen and oxygen to exist together with radioactive gases in the waste gas treatment system.

This report summarizes results from a study which had as its main objective the evaluation of problems associated with the existence of explosive gas mixtures in PWR waste gas systems. The following tasks were accomplished:

- Information on existing waste gas systems was obtained from six operating PWRs through visits and discussions with plant personnel.

- Data on the effect of initial pressure on flammability limits for hydrogen/oxygen/nitrogen mixtures has been collected and summarized. In addition, recent studies on the flammability and detonability of hydrogen/air mixtures has been reviewed.

- An evaluation of commercially available hydrogen and oxygen gas monitoring systems and instrumentation has been performed.

The results of this study are presented in this report. More detailed information can be derived from the references and appendices. Section 2 gives a general discussion of waste gases, flammability, and PWR waste gas systems. Section 3 discusses the results of the plant visits. Section 4 gives a discussion and qualitative evaluation of the risk for explosion. In Section 5, a review of results from recent investigations of combustion and detonation of hydrogen/air mixtures is given, while Section 6 addresses existing commercial instrumentation for on-line monitoring of hydrogen and oxygen. In Section 7, overall conclusions are given while Section 8 makes recommendations.

2. PWR WASTE GASES, FLAMMABILITY AND WASTE GAS SYSTEMS

2.1 Waste Gases

In the closed, recirculating, primary coolant system of a PWR, various gases are produced as a result of the fission process or are introduced to control water chemistry. The gases produced as a direct result of the fission process are the noble gases, xenon and krypton, and the halogens. These gases are highly radioactive and the fuel cladding normally keeps them contained within the fuel. However, some gas may enter the coolant from small leaks in the cladding (cladding pinhole, imperfect seal welds). For design purposes, it is usually assumed that 0.12% of the fuel pins leak in this fashion. In addition, there are usually trace quantities of uranium present on the exterior fuel cladding surface which directly emit small amounts of gases to the coolant.

Other gases are also produced in the coolant water due to the high radiation fields present in the fuel region. These are primarily non-radioactive hydrogen and oxygen produced by radiolytic decomposition of water, as well as radioactive N-16 and N-17. The latter two have such short half-lives (seven seconds and four seconds, respectively) that they are not of concern. At the operating temperature and pressure of a PWR, oxygen is corrosive to reactor internal materials and is partially scavenged by the deliberate introduction of excess hydrogen as part of the control of water chemistry. The addition of excess hydrogen (~ 25 cm^3/Kg coolant) shifts the equilibrium of the reaction $2H_2O \rightleftarrows 2H_2 + O_2$ toward the water side of the reaction.

During reactor operation, a small fraction of the primary coolant water is continuously removed (~5 to 75 gpm) via a letdown line. This water is cooled and letdown in pressure to allow processing (typically 3 to 5 gpm) then returned to the primary system. The processing maintains control of water chemistry via the Chemical and Volume Control System (CVCS), removes boron for reactivity control via the boron recovery system, and removes radioactive materials via the radwaste system. The pressurizer system is a second source of water and gas. The pressurizer and letdown systems contain various liquid tanks, evaporators, and/or gas strippers at pressures generally near 1 atmosphere. Dissolved gases are released from the liquid into the vapor space in these liquid tanks or in the gas strippers. Each tank has a hard-piped line to a waste gas header which sends them to the Waste Gas System (WGS). Figure 1 is a schematic diagram of a typical reactor primary coolant system illustrating the major sources of gases. An inert cover gas, usually nitrogen, is maintained throughout most of the tanks and piping to dilute the hydrogen and oxygen and to allow tank levels to fluctuate. An exception is the Volume Control Tank (VCT), which is part of the CVCS. At the VCT, hydrogen gas is added to the primary coolant to control corrosion. Hydrogen is present in the VCT at a gas to liquid volume ratio of about two to one. Water is sprayed into the vapor space of the VCT to pick up the hydrogen. This hydrogenated water is then returned to the primary coolant system.

The relative composition of gases entering the waste gas header varies with the operational mode of the plant. The major gases are nitrogen, hydrogen, and oxygen together with a comparatively small volume of the radioactive noble gas fission products and tritium. The nitrogen/hydrogen ratio can vary over nearly the entire range but is typically 95/5% to 5/95%. Oxygen is usually $\lesssim$ 2% during reactor operation, but can exceed 5% following shutdown for refueling.

As mentioned above, a waste gas system is incorporated in order to exert control over the amount of radioactive gases released from the plant. The waste gas system is designed to provide sufficient storage or hold-up time to allow the important shorter lived radioisotopes to decay. Table 1 lists the half lives of the noble gas nuclides for those gases having half lives greater than one minute. Also given are the calculated values of their cumulative fission yields in atoms per 100 fissions for U-235 thermal fission. The last column gives the mean energy emitted per unit of cumulated activity, Δ in Rads/hr per μCi/g. For an infinite, homogenous medium in which a radioactive source is uniformly dispersed with a concentration of 1 μCi hr/g, Δ gives the absorbed dose in rads. This column thus gives an idea of the relative hazard from being immersed in a cloud of the gas. The values given do not include the effects of daughter activities. It is clear from the table

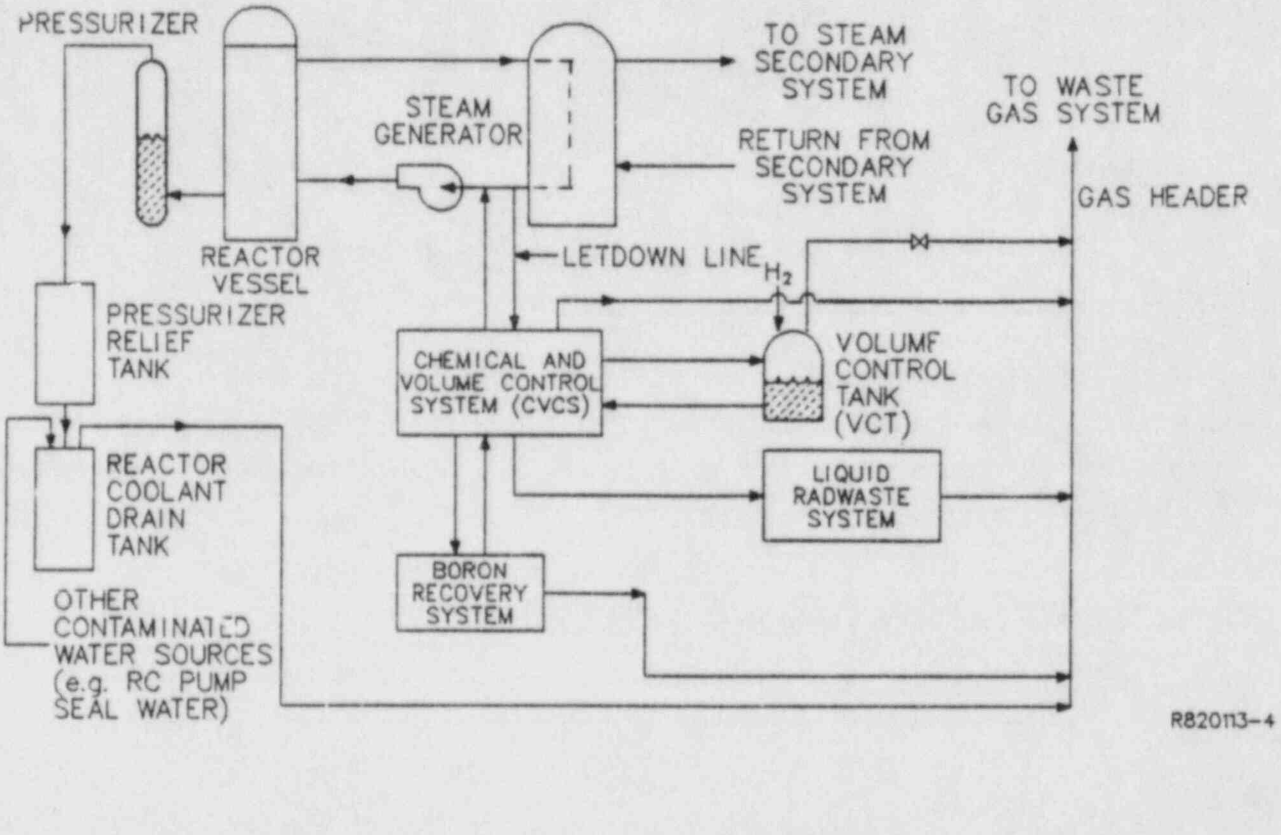

Figure 1. Schematic of a Typical Reactor Primary Coolant System.

TABLE 1. NOBLE GAS FISSION PRODUCTS WITH HALF-LIVES GREATER THAN ONE MINUTE

Nuclide	Half-life	Cumulative Fission Yield[a]	Δ(g-Rad/μCi Hr)[b]
Kr-83m	1.83 Hours	0.5374	0.0868
Kr-85m	4.48 Hours	1.1310	0.1370
Kr-85	10.72 Years	0.288	0.7410
Kr-87	76.30 Minutes	2.544	4.4858
Kr-88	2.84 Hours	3.612	4.9018
Kr-89	3.16 Minutes	4.718	6.4783
Xe-131m	11.84 Days	0.040	0.3460
Xe-133m	2.19 Days	0.190	0.4936
Xe-133	5.25 Days	6.703	0.4031
Xe-135m	15.30 Minutes	1.086	1.1206
Xe-135	9.11 Hours	6.555	1.2011
Xe-137	3.82 Minutes	6.139	4.1213
Xe-138	14.13 Minutes	6.443	3.6803

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a. M. E. Meek and B. F. Rider, Compilation of Fission Product Yields, Vallecitos Nuclear Center, NEDO 12154-1-1974, (atoms per 100 fissions for U-235 thermal fission).

b. David C. Kocher, Radioactive Decay Data Tables, DOE/TIC-11026, 1981.

that a hold-up or retention time of 30 to 45 days will reduce the total activity, except for Kr-85, by a factor of ten or more. For typical noble gas mixtures, a one-day holdup provides a reduction in activity of about a factor of 15 for krypton mixtures, while for typical xenon mixtures, twenty days of holdup provide a similar reduction in activity. Typically, design storage time of about 45 days is provided.

2.2 The Flammability Problem

In providing storage for the radioactive gases, the waste gas system also contains hydrogen, nitrogen, and oxygen. Mixtures of hydrogen and oxygen are flammable and/or detonable within certain concentration envelopes. Thus, the effects on the WGS must be analyzed. Historically, the usual solution has been to dilute the hydrogen/oxygen gas mixture with nitrogen until the mixture is below the flammable limit. The only other control measure generally available is to release the waste gas with additional air dilution to the atmosphere. There are basically two different plant operation regimes that affect the hydrogen to oxygen ratio. During power operation, hydrogen in the WGS is typically 1 to 3% while oxygen is usually $\leq$ 0.1%. Where controls are minimal however, concentrations as high as 46% hydrogen and 22% oxygen have been observed (NRC Private Communication). At shutdown for refueling, the system is purged to remove hydrogen. These modes are hydrogen (fuel) rich (compared to oxygen). The second regime often occurs at startup after refueling. During refueling, the reactor vessel head has been removed, various tanks may have been opened, or subsections opened for maintenance. These operations allow ambient air to enter the system. At startup, there is very little hydrogen initially present, but there is significant oxygen. This is an "oxygen rich" regime which can contain 5 to 20% oxygen.

Thus, in a PWR, there is excess hydrogen present during reactor operation and only a fraction of the resident gases are subject to treatment via the letdown system. The composition ranges can change significantly in going from one mode of plant condition to another. Typical flows are < 10 scfm. Instead of being released as produced, the gases are quite often simply stored in tanks. One can, therefore, build up an inventory of flammable or detonable mixtures of gases. A fire or detonation within the waste gas system could result in the uncontrolled release of radioactive gases. This could result in radiation doses to plant personnel and members of the public. Consequently, means are needed to either preclude or significantly reduce the likelihood of formation of flammable mixtures.

On the other hand, in a BWR, these gases are removed from the main condenser via the steam jet air ejector and processed. The processing usually consists of a recombiner to remove the hydrogen followed by large charcoal beds (12 to 40 tons) to hold up noble gases. The gases have relatively constant composition ratios of hydrogen, oxygen, and nitrogen, and the off-gas system handles the entire amount of gas as produced. These off-gas systems are once-through systems with no accumulation or storage of flammable gases. Thus, the flammability hazard is limited to the gas being processed. Typical flow rates and concentrations into the system of a 3500 MWt power plant are 100 scfm; 50% hydrogen, 30% oxygen, 20% nitrogen, respectively at a pressure of 1 atmosphere. Since essentially all the flammable gases are removed as produced, there is little chance of them accumulating in chemistry control or liquid radwaste subsystem tanks. In addition, when the reactor is shut down for refueling, there is no excess hydrogen to handle since, at present, BWRs do not use it to control oxygen.

In BWRs, most off-gas systems are designed to handle the overpressures due to a hydrogen explosion. There have been 29 explosions in 100 reactor operating years between 1971 and 1977 in BWR systems[1]. The radiological consequences in all cases were negligible and only minor plant damage or personnel injury occurred. This type of event is, therefore, considered to be a high-probability, low-consequence accident. In many PWRs, the gases are stored under pressure (~100 psig). The inventory of stored gases can be relatively high and generally PWR waste gas systems are not designed to contain explosion overpressures. Fires or explosions in PWRs have, therefore, been considered of low probability but of potentially high consequence. In some 200 cumulative reactor years prior to 1981, there had been no explosions. The only fire known to have occurred in a PWR waste gas system occurred in 1981[2]. It started in a recombiner in a system not designed to withstand explosions. The radiological consequences were well below allowed limits and relatively minor damage to the system occurred, although the recombiner was rendered inoperable.

The control of flammable and explosive gas mixtures has received regulatory attention as part of the total effluent control in the model Radiological Effluent Technical Specifications (RETS)[3].

2.3 Waste Gas Systems

In a PWR, the gases stripped from the primary system and the waste gases from the various other systems are sent via header pipes to the WGS. Waste gas systems have several designs. Functional block diagrams for four design approaches are illustrated in Figure 2. The Type A system is discussed in more detail since it is one of the most common systems used.

Type A
Fig. 2a

This is the simplest design. Gases from the waste gas header are compressed (typically to ~100 psig) and stored in waste gas decay tanks (WGDTs). The number and volume of WGDTs is plant specific, but typically the number of tanks range from three to six and the volume of each tank varies from 100 to 600 ft^3. Figure 3 is a more detailed block diagram of such a WGS. Two compressors are used for redundancy, and usually a separate surge tank is provided. This type of system is designed to maintain pressure slightly above atmospheric at the input to the compressors. The slight positive pressure is intended to prevent air in-leakage in the event of system leaks. The type of compressors usually used are positive displacement with either diaphragm or water sealed and cooled impeller pumps. Compressor operation can be automatic or manual, but all have provisions for automatic shut off if the input pressure falls below a preset level, typically 0.5 to 1 psig. In manually operated systems, only one compressor is used at a time unless the gas flow becomes too high. In automatic systems, the compressor startup pressure thresholds are set at slightly different values so that the second compressor does not start unless the first unit cannot handle the flow. Typical compressor flow rates are 2 to 4 scfm at discharge pressures of ~80 to 100 psig. Some discharge pressures can be as high as

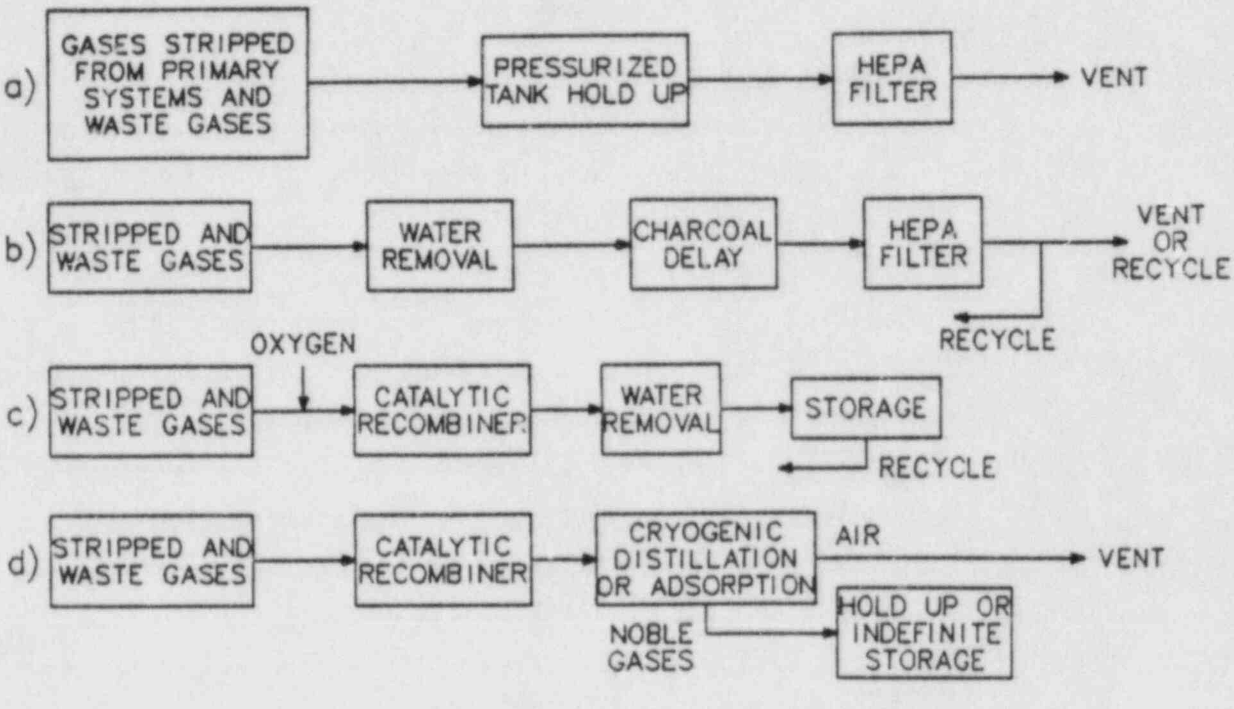

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Figure 2. Block Diagrams for Four WGS Designs.

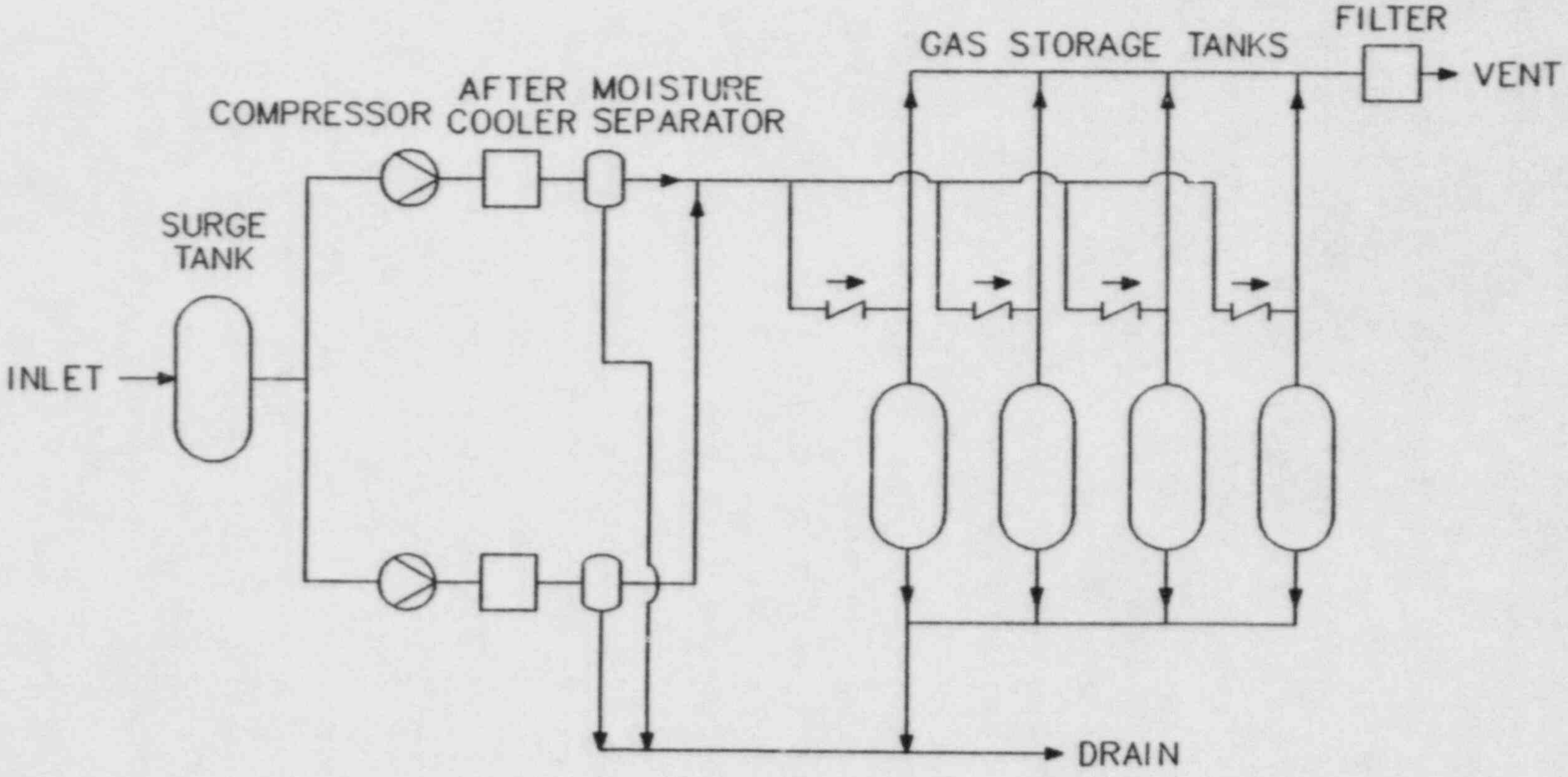

Figure 3. Compressed Gas Storage System Flow Diagram.

200 psig. Bypass from the compressor output side to the input side is provided to maintain positive input pressure; nitrogen backup from an external source is also provided.

Type B
Fig. 2b

This type of system, a low-pressure system, does not store gases in tanks. Holdup of noble gases is provided by beds of activated charcoal, with the hydrogen, oxygen, and nitrogen simply flowing through the system. Provision for recycle can be incorporated for use in the event that noble gas activity levels are too high. Moisture removal from the gases is provided because the ability of charcoal to provide holdup (dynamic adsorption coefficient) decreases with increasing moisture loading. The holdup time provided depends on the mass of the charcoal, the flow rate, and the temperature dependent dynamic adsorption coefficient. At a typical continuous flow rate of 2 cfm and a bed temperature of 80°F, two tons of charcoal provide about 1 day of holdup for krypton and 24 days for xenon. Systems of this type may also incorporate a catalytic converter to remove hydrogen and oxygen.

Type C
Fig. 2c

This system is essentially similar to Type A in that compressed gases are stored. However, it incorporates a catalytic recombiner to remove hydrogen prior to storage. This system is designed to store noble gases indefinitely (i.e., zero release over the life of the plant). Note that a recycle back to the input of the recombiner is provided so that hydrogen removal is continuous. Control of the amount of oxygen added to react with the hydrogen is maintained by measurement of the amount of unreacted hydrogen at the outlet of the moisture removal section. This type of system is designed mainly to remove hydrogen (i.e., the hydrogen "rich" mode prior to storage in waste gas decay tanks).

Type D
Fig. 2d

This system is similar to Type C in that a recombiner is incorporated to remove oxygen. Cryogenic cooling of the gases allows for selective condensation of both krypton and xenon while any oxygen, nitrogen, and hydrogen remain gaseous. In order to provide selective condensation at 1 atmosphere the system must be maintained at a temperature above the oxygen boiling point (90.19°K) but below that of krypton (114.8°K). An operating temperature near 100°K (-280°F) is typical. The liquified xenon and krypton can then be stored.

A variation to this type of system uses a cryogenically cooled charcoal bed. This provides an adsorption bed for condensing noble gases while allowing the other gases (almost entirely nitrogen) to pass through the bed. Periodically (once or twice a year), the charcoal bed is regenerated by warming it to release the noble gases. These gases (primarily Kr-85) can then be compressed and stored permanently in high-pressure bottles.

3. PWR PLANT SURVEY RESULTS

Six operating, commercial PWR power plants were surveyed to obtain information on their WGSs and operating experience. Information was also obtained on the instrumentation used to monitor hydrogen and oxygen concentrations in the WGS. The information obtained was based on the plant Final Safety Analysis Report (FSAR), and review of the WGS piping and instrumentation diagrams. Discussions with plant operations' personnel dealt with specific WGS experience and problems, while discussions with the chemistry and maintenance group dealt with instrumentation experiences and problems. Both on-line and off-line (Laboratory) monitoring systems were discussed.

A summary of the results from the PWR plant visits and personnel discussions is given in the following sections. Table 2 summarizes information on the plant's WGSs, while Tables 3 and 4 summarize the plant instrumentation. In some cases (2 of 6), sufficient information was available to generate process diagrams.

Monitoring of gases in PWR WGSs is done to measure the levels of radioactivity present and to determine the concentrations of hydrogen and/or oxygen. Instrumentation for monitoring hydrogen and oxygen can be on-line or off-line. In the latter case, a grab sample is usually taken to the rad chem laboratory for analysis. All plants visited use off-line gas chromatograph (GC) instrumentation to perform hydrogen, oxygen, and nitrogen analysis. Some plants use on-line monitors as well. The usual off-line instrument is a GC. The off-line laboratory instruments are research grade instruments which are quite accurate and reliable as long as adequate calibration standards are used and the instruments are maintained. On-line instrumentation usually uses a paramagnetic sensor for oxygen and a thermal conductivity sensor for hydrogen. See Tables 3 and 4 for actual instruments used in the plants surveyed. Table 5 summarizes the gas concentration information (ranges and extremes) obtained at the plants visited.

TABLE 2. PLANT SURVEY SUMMARY: WASTE GAS SYSTEMS

			3				
Plant Number	1	2	Unit-1	Unit-2	4	5	6
WGS Type	A	A	A	A	D	C	C
Number of Reactors	1	2	1	1	1	2	2
Number of WG Systems	1	1 for two units	1	1	1	2	1
Explosion Proof Design	No	No	No	No	No	No	No
Piping Material	Stainless Steel	Stainless Steel	Retrofit with St. Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel
Surge Tank	1431 gal Cast iron	None	26.4 ft^3 Carbon Steel	10 ft^3 Rubber lined Carbon Steel	125 ft^3 30 psig max	None	14.7 ft^3
<u>Waste Gas Compressors</u>							
Number	2	2	2	2	2	2	2
Type	Diaphragm	Nash Rotary Vane	Diaphragm	Diaphragm	Diaphragm	Nash Rotary Vane	Diaphragm
Design Pressure (psig)	200	150	100	350	100	150	150
Design Discharge Temperature (°F)	245	110	120 to 170	150 to 350	150	120	120
Flow Rate (scfm)	16	2-3	4.4	20	2.5	40	1.5
Operation	Automatic	Automatic	Automatic	Automatic	Automatic	Automatic	Automatic
Minimum Input Pressure	0.5 psig	0.5 psig	0.5 psig	0.5 psig	0.5 psig	1.0 psig	0 psig

TABLE 2. Continued

			3				
Plant Number	1	2	Unit-1	Unit-2	4	5	6
Waste Gas Decay Tanks							
Number	3	6	4	3	3	8	2
Volume (ft^3)	132	525	320	300	125	600	462
Design Operating Pressure (psig)	115	110	123	150	100	150	115
Design Max Pressure (psig)	225	150	132	380	150		175
Design Max Temperature (°F)	220	150	125	250		180	200
WGDT Discharges	15 to 20/yr	50 to 60/yr	Only during Refueling	One during Refueling	1 to 3/wk	Only at Startup after Refueling	6 to 12/yr
Recombiner	None	None	None	None	Yes	Yes	Yes
Number per WGS					1	1	1
Design Recombination Range					0 to 3% O_2 0 to 6% H_2	0 to 3% O_2 0 to 6% H_2	0 to 2% O_2 0 to 4% H_2
Pressure					10 psig	10 psig	7 psig
Operation					Batch	On-line	Has never been used
Absorber	None	None	None	None	Yes	None	None
Material					Charcoal		
Mass					~1000 lbs		
Operating Temperature					-275°F		

TABLE 2. Continued

			3				
Plant Number	1	2	Unit-1	Unit-2	4	5	6
Main WGS Problems	None after Rebuilding	Cover Gas, Leaks, Moisture	Moisture, Corrosion, Leaks, System Secured	System Secured	Fire in WGS 7/81	Moisture, Improper line locations, Getting the recombiner to operate properly	Obtaining Replacement Parts

TABLE 3. PLANT SURVEY SUMMARY: ON-LINE GAS ANALYZERS

Plant Number	Gas	Make & Model	Number	Principle	Range	Alarm Setpoint	Location	Remarks
1	H_2	None						
	O_2	None						Plan to Install Redundant O_2 Monitors
2	O_2	MSA Model 802	1	Paramagnetic		2%	Sequenced to 14 sample locations including WGDT's, RCDT, VCT, SRST	Used for both reactors. Samples automatically.
	H_2	MSA Model T-3	1	Thermal Cond.				
3 Unit 1		Hays Gas Analyzer					Auto sequenced to 9 sample locations including Surge Tank and 4 WGDT's. Usually on Surge Tank	One alarm for both instruments.
	O_2	Model 632-II	1	Paramagnetic	0 to 5%	3%		
	H_2	Model 643-E	1	Thermal Cond.	0 to 5%	3%		
3 Unit 2		Beckman Gas Analyzers:					Loop A: 7 locations VCT, WGDT's (3), Surge Tank, Degasifier, Containment vent for H_2 and O_2	Added redundant O_2 system is planned.
	O_2	Model F3M3	1	Paramagnetic	0 to 5%	3% (Loop A)		
	H_2	Model 7C	2	Thermal Cond.	0 to 5%	5% (Loop B)	Loop B: 4 locations, holdup tanks (3), spent resin tank. H_2 only.	
	O_2	Model F3	1	Paramagnetic	0 to 5%		WGS compressor discharge.	

TABLE 3. Continued

Plant Number	Gas	Make & Model	Number	Principle	Range	Alarm Setpoint	Location	Remarks
4	H_2	None					None on Compressor WGDT Portion of WGS.	
	O_2	None						
	O_2	Anacon Model 75	1	Electro Chemical Cell	0 to 10 0 to 100, 0 to 1000 ppm	5 ppm	Between water separator and dryer downstream of O_2 recombiner.	
5	H_2	Bendix Catalytic Combustion Analyzer Model B-1631-TM	4 per nuclear unit (2 recomb. per unit)	Catalytic element	0 to 6% 0 to 15%	Hi-6% Hi-Hi - 9%	One before the preheater to the recombiner. One after the recombiner downstream of the of the phase separator.	To prevent overheat- of recombiner. To operate on slightly H_2-rich mode to assure complete combustion of O_2.
	O_2	Teledyne Analytical Instrument Model 327	1 per recombiner	Micro-fuel Cell (electrochemical transducer)	0 to 3%		Located upstream of the catalytic reactor of the recombiner.	To limit O_2 feed gas to a maximum of 3%.
5	O_2	Teledyne Instrument Model 317	1 per recombiner	Micro-fuel cell (electrochemical transducer)	0 to 15 ppm		Located downstream of the phase-separator after the recombiner.	To warn of unburned oxygen concentration.

TABLE 3. Continued

Plant Number	Gas	Make & Model	Number	Principle	Range	Alarm Setpoint	Location	Remarks
6	O_2	Bendix OA 137	1	Paramagnetic	0 to 1%, 0 to 5%	Alarm at 2%	WGS Compressor Section	
	H_2	Bendix 400 LX	1	Thermal Cond.	0 to 100%	None	WGS Compressor Section	
	O_2	Beckman F-3M3-1AA	2	Paramagnetic	0 to 5%	Alarm at 3%	Recombiner Outlet	
	O_2	Beckman F-3M3	1	Paramagnetic	0 to 5%	Alarm at 4%	Recombiner Recycle Compressor Suction Heater	
	O_2	Hays 632-II	1	Paramagnetic	0 to 1%	Alarm at 0.1%	Gas Stripper Surge Tank	
	H_2	Beckman 7C	2	Thermal Cond.	0 to 500 ppm	Alarm at 490 ppm	Recombiner Outlet	
	H_2	Beckman 7C	2	Thermal Cond.	0 to 4%	Alarm at 3.6%	Recombiner Recycle Compressor Suction Header	

TABLE 4. PLANT SURVEY SUMMARY: OFF-LINE GAS ANALYZERS AND SAMPLING

Plant	Type	Make & Model[a]	Conditions[b]	Sampling Schedule & Remarks
1	Gas Chromatograph	Perkin-Elmer Sigma-3	Helium, Molecular Sieve, 40°C, TC	Active decay tank only at time of discharge.
2	Gas Chromatograph	Carle III H Gas Partitioner	Helium, Molecular Sieve, 57.5°C, TC	Once/week from operating WGDT. Provisions for other sample points. Can be used either for grab samples or can sample automatically.
3				
Unit 1	Gas Chromatograph	Fisher Scientific Gas Partitioner 1200	Argon, Molecular Sieve, 30°C, TC	WGDT grab sampled as needed for discharge. Provisions exist for other grab samples.
Unit 2	Gas Chromatograph	Partitioner 1200	Same	WGDT grab samples as needed. Provisions exist for other gas samples.
4	Gas Chromatograph	Carle Model III	Helium, or Argon; Molecular Sieve 80°C, TC	WGDT grab sampled when up to pressure just before processing through recombiner/cryogenic unit.
5	Gas Chromatograph	Fisher Scientific Gas Partitioner 1200 (1 per reactor)	Argon, Molecular Sieve, 30°C, TC	WGDT's grab sampled on an as needed basis. Provisions to sample VCT exist.
6	Gas Chromatograph	Fisher Scientific Gas Partitioner 1200	Argon, Molecular Sieve, 50°C, TC	WGDT Sampled at time of discharge. Initiating a routine once/month WGDT Grab Sample Program.

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a. Plant 2 has purchased a Perkin Elmer Sigmer 115 GC; plant 4 has purchased a Hewlett Packard 5840A GC.

b. Conditions given are carrier gas, column type, temperature, detector; TC = thermal conductivity.

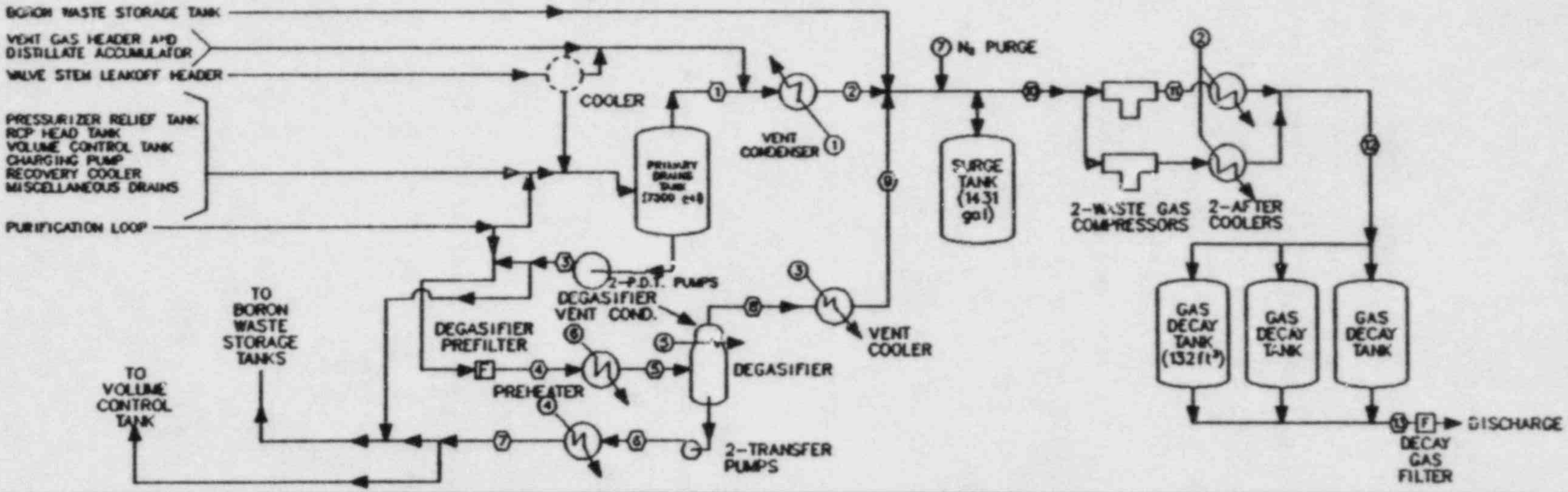
TABLE 5. SUMMARY OF PLANT GAS CONCENTRATION INFORMATION

Plant	Gas	Range (%)	Extremes
1	High H_2, O_2	1 to 3	7% O_2
2	High H_2, O_2	< 1	3% O_2
3 Unit-1	H_2, O_2	> 5, < 0.5	11.7% H_2, 6.1% O_2
Unit-2	H_2, O_2	10 to 13, 1.7 to 2.8	~3% O_2
4	High H_2, O_2	< 1	3.8% O_2
5	H_2, O_2	4 to 6, 0.2	< 7% H_2 Unit-1 < 18% H_2 Unit-2
6	H_2, O_2	5 to 7, < 4	9% H_2, 5% O_2

3.1 Plant Number 1

This is a single unit 600 MWe 4-loop Westinghouse plant which began commercial operation in 1968. The WGS is a positive pressure Type A system (i.e., gas compression and storage, without a recombiner). The WGS consists of a degasifier, a 191 ft^3 surge tank, two waste gas compressors (200 psig discharge) and three 132 ft^3 waste gas decay tanks (WGDTs). A schematic is shown in Figure 4. WGS inputs are from the boron waste storage tank, the vent gas header and distillate accumulator, valve stem leak off, the purification loop, and the 7500 gal. primary drains tank. All plumbing and tanks are stainless steel, with ball valves used throughout. The present WGS was installed in 1975. Prior to that time, the plant used a diaphragm type surge tank and carbon steel plumbing. Leaks in the surge-tank diaphragm and moisture-based corrosion problems were two reasons for building the present WGS which was accomplished as part of a general upgrade of the entire plant radwaste system. The WGS compressors automatically start at 1.5 psig (increasing input pressure) and shut off at 0.5 psig. Discharge of gaseous contents take place at pressures of 200 psig or less. Nitrogen is used as a cover gas and for dilution purposes. The plant has not had a WGS fire. There are no known potential ignition sources.

The plant has no on-line instrumentation for analysis of hydrogen or oxygen in the WGS. Present plans call for installation of on-line oxygen analyzers to monitor the outlet of each waste gas compressor. Analysis of gases is accomplished using grab samples which are analyzed off-line using the chemistry lab GC. Sampling and analysis of hydrogen and oxygen concentrations is done only prior to discharge of a WGDT. Typically, a tank is discharged after a 2 to 4 week decay depending on plant operation. Discharge is typically 15 to 20 tanks per year. Oxygen concentration is typically in the 1 to 3% range. In one instance, concentrations of 7.9% hydrogen and 7.3% oxygen were measured. This was atypical and it was believed that the high oxygen value was due to sample contamination and the tank was discharged as planned.



PROCESS LOCATION	1	2	3	4	5	6	7	8	9	10	11	12	13
FLUID	H_2/FISSION GAS	H_2/FISSION GAS	BORATED WATER	BORATED WATER	BORATED WATER	BORATED WATER	BORATED WATER	H_2/FISSION GAS	H_2/FISSION GAS	H_2/FISSION GAS	H_2/FISSION GAS	H_2/FISSION GAS	H_2/FISSION GAS
FLOW	15.9 lb/hr	15.9 lb/hr	200 GPM	1x10³ lb/hr	200 GPM	210 GPM	200 GPM	15 lb/hr	15 lb/hr	18 SCFM(MAX)	18 SCFM(MAX)	18 SCFM	40 SCFM
PRESSURE	0.853 psig	0.853 psig	220 ft H_2O	45 psig	2.0 psig	140 psig	95 psig	1 psig	1 psig	1 psig	225 psig(MAX)	200 psig(MAX)	0.5 psig
TEMP	140°F	120°F	120°F	115°F	219°F	219°F	122.5°F	159°F	115°F	80–120°F	245°F	---	---
ACTIVITY	---	---	---	---	---	---	---	---	---	---	---	---	---
CHEMICAL	---	---	---	---	---	---	---	---	---	---	---	---	---

UTILITY LOCATION	1	2	3	4	5	6	7
SERVICE	SERVICE WATER	WATER	COMP COOL WATER	COMP COOL WATER	COMP COOL WATER	STEAM	N_2 PURGE GAS
FLOW	375 lb/hr	2 gpm	3x10³ lb/hr	3.5x10³ lb/hr	5.3x10⁴ lb/hr	1.2x10⁴ lb/hr	---
TEMP (ΔT)	85–100°F	---	85–95°F	95–122.5°F	95–135°F	338°F(MAX)	---
HEAT RATE	---	---	1.45(10⁴)btu/hr	9.6(10⁴)btu/hr	2.1(10⁶)btu/hr	1.2(10⁷)btu/hr	---

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Figure 4. Process Diagram of Plant Number 1 Waste Gas System.

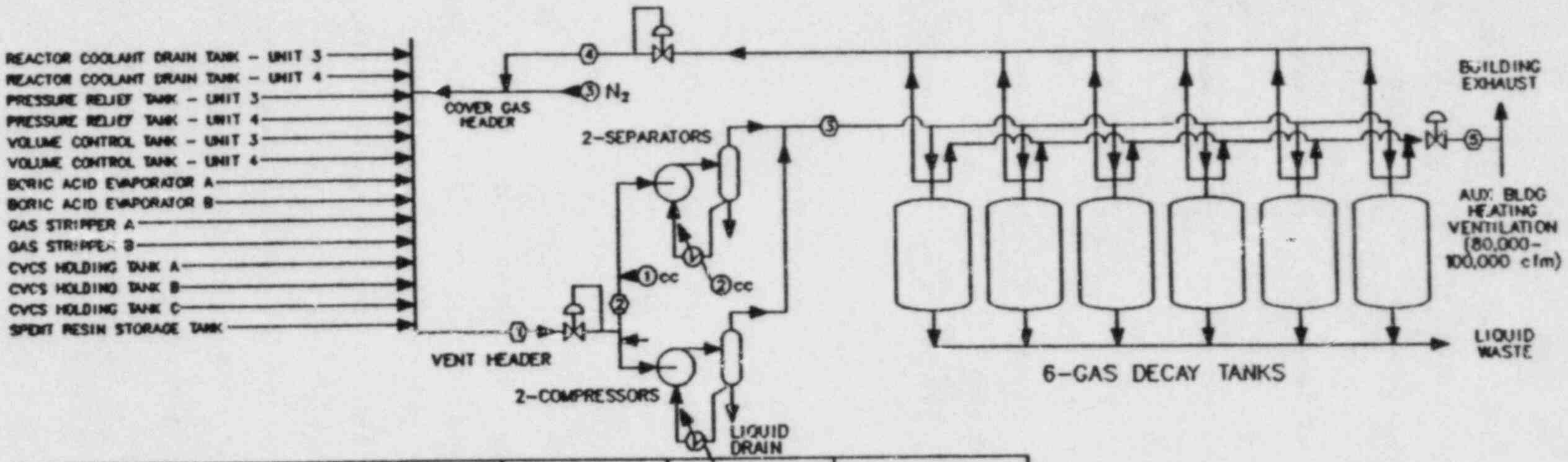
3.2 Plant Number 2

This station has two nuclear units, each of 666 MWe Westinghouse 3-loop design. A single WGS services both units. It is a Type A system fabricated of stainless steel. The system consists of two compressors, each with a moisture separator and six 525 ft^3 decay tanks (see Figure 5). One of these decay tanks is usually used to hold the nitrogen cover gas. Operating pressure is nominally 150 psig. The system was not designed to contain a hydrogen explosion. The compressors are rotary vane type with water seals. Gas inputs to the system are:

- Reactor coolant drain tanks for both units
- Pressure relief tanks for both units
- Volume control tanks for both units
- The chemical and volume control system holdup tank
- Spent resin storage tank
- Two boric acid evaporators
- Two gas strippers.

Compressor operation, which is automatic, starts at an input pressure of 2.25 psig and shuts off at 1.85 psig. Below 0.5 psig, nitrogen gas is supplied to maintain a positive gas pressure. This plant is located in a humid area and the main problem with the WGS has been moisture. On two occasions, the compressor has overflowed into the vent header, necessitating maintenance. Moisture has also caused problems in pressure control valve pneumatic lines. 50 to 60 WGDT discharges occurred in 1981, but are expected to be less in the futur[illegible] to system repairs.

This plant has an extensive system of on-[illegible]e gas analyzer capability, as well as laboratory equipment. The on-li[illegible]em consists of analyzers, moisture removal equipment, and miscellaneous valves, instruments, and tubing. The system receives gas samples through a sequencer which can sample 14 plant locations:



PROCESS LOCATION	①	②	③	④	⑤
FLUID	WASTE GAS	WASTE GAS	WASTE GAS	WASTE GAS	WASTE GAS
FLOW	6–20 cfm	6–20 cfm	2–3 cfm	3–10 cfm	20–80 cfm(1)
PRESSURE: (psi) DESIGN OPER	 0.5–1.65 0.5–1.65	 0.5 0.5	 150 3–110	 0.5–1.0 0.5–1.0	 15–100 ATMOS.
TEMP.(°F)	93	86	97	91	97
ACTIVITY (μCi/cc)	$\simeq 10^{-2}$	$\simeq 10^{-2}$	$<10^{-2}$	$\simeq 10^{-2}$	$\simeq 10^{-2}$
CHEMICAL (% vol) H_2 N_2 O_2	 5–95 95–5 <3	 5–95 95–5 <3	 5–95 95–5 <3	 5–95 95–5 <3	 5–95 95–5 <3

UTILITY LOCATION	①	②	③
SERVICE	COMPCOOL WATER	COMPCOOL WATER	N_2 PURGE GAS
FLOW	20 cfm	20 cfm	3–10 cfm
PRESSURE (psi)	---	---	0.5
TEMP.(°F)	87	89	80
TEMP.OUT	90–110	N/A	---

(1) ANNUAL DISCHARGE VOLUME IS PRESENTLY 50 – 60 TANKS (ABOUT $2.7(10^5)FT^3$)

R820117–4

Figure 5. Process Diagram of Plant Number 2 Waste Gas System.

- Reactor coolant drain tank of each unit (2)
- VCT of each unit (2)
- Pressure relief tank of each unit (2)
- Spent resin storage tank (1)
- Gas stripper (2)
- CVCS holdup tanks (3)
- Any preselected decay tank (1)
- WGS discharges to the plant ventilation exhaust system (1)

The sequencer can operate in an automatic mode, extracting up to 20 samples per cycle. Processing requires five to six minutes per sample. The off-line analyzer can also be used in an on-line configuration and the system has provisions to automatically extract samples. In addition, grab samples are possible. The on-line analyzers are shown in Table 3. Typically, the oxygen concentration is less than 1% and on rare occasions, has been as high as 3%. Nitrogen/hydrogen concentrations vary from approximately 95%/5% during startup and shutdown when nitrogen is used to purge the system to 5%/95% during reactor operation. This plant has never had a WGS fire and there are no known potential ignition sources.

3.3 Plant Number 3

This is a two-unit plant, one provided by Babcock and Wilcox and the other by Combustion Engineering, each having two loops. Unit 1 generates 875 MWe and Unit 2 generates 941 MWe. Units 1 and 2 began commercial operation in 1974 and 1980, respectively. Each unit has its own WGS. Both WGSs are Type A compressed gas storage. Each consists of a vacuum degasifier, surge tank, two compressors, moisture separators, and decay tanks. Units 1 and 2 have four and 3 decay tanks, respectively and are constructed of carbon steel. They are not designed to withstand explosion overpressures. Some details, specific to each unit, are given below.

Unit 1

Figure 6 shows a flow schematic for the WGS of Unit 1. The WGS has an on-line gas analyzer system with an automatic sequencer to select samples. The analyzer accepts inputs from:

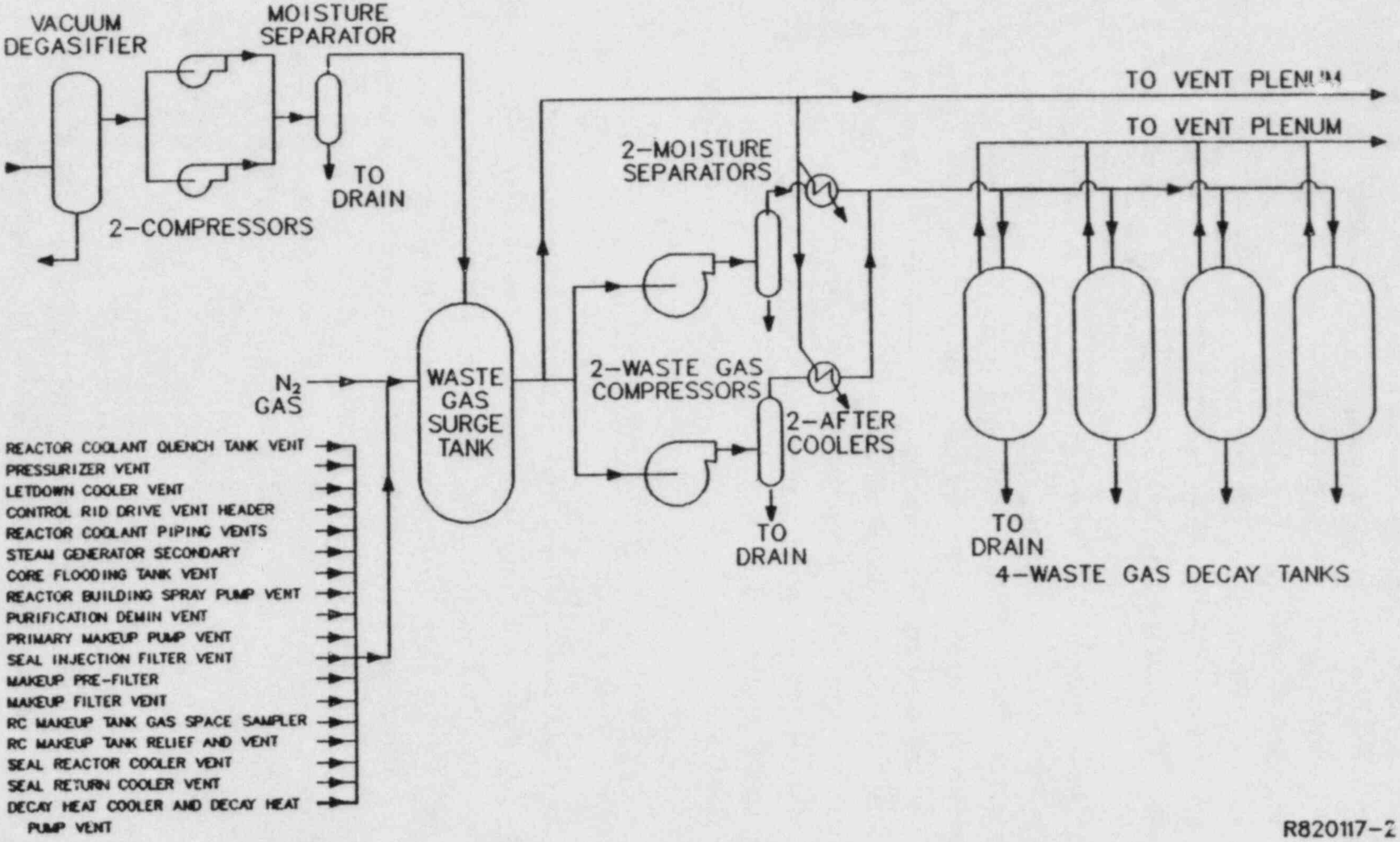


Figure 6. Flow Schematic of Plant Number 3, Unit 1 Waste Gas System.

- Waste gas surge tank
- Dirty waste drain tank
- Auxiliary building equipment drain tank
- Clean waste receiver tanks (4)
- Primary coolant quench tank
- Waste gas decay tanks (4)

Hydrogen/oxygen concentrations are monitored continuously from the waste gas surge tank (WGST). There are plans to install a second hydrogen/oxygen analyzer in parallel with the existing system for backup. Gas analyses typically indicate <0.5% oxygen and >5% hydrogen during normal operation. However, one grab sample in 1980 indicated an oxygen concentration of 11.7% and a hydrogen value of 6.1%. The Unit 1 WGS has not been used frequently enough to have a WGDT discharge (only during refueling when they need to vent the nitrogen cover gas). The reasons for lack of discharge are:

- Good fuel
- Non-use of the radwaste evaporator
- Non-use of the boric acid evaporator
- The Volume Control Tank (reactor coolant makeup tank) vent not feeding into the WGS header
- No degassing of the system during normal operation
- Collection header exhaust fan in auxiliary building used to exhaust low activity, aerated gas mixtures.

The WGS for Unit 1 leaks and is undergoing retrofit. To date, the entire Unit 1 WGS has been secured and has a nitrogen cover gas of ~3 in. of water (~0.1 psig). About 95% of the piping has been replaced with stainless steel and old valves have been replaced with new.

Unit 2

A flow schematic of this system, showing the gas input sources, is given in Figure 7. The compressors operate automatically based on the pressure in the WGST. One of the compressors starts at 4 psig and shuts

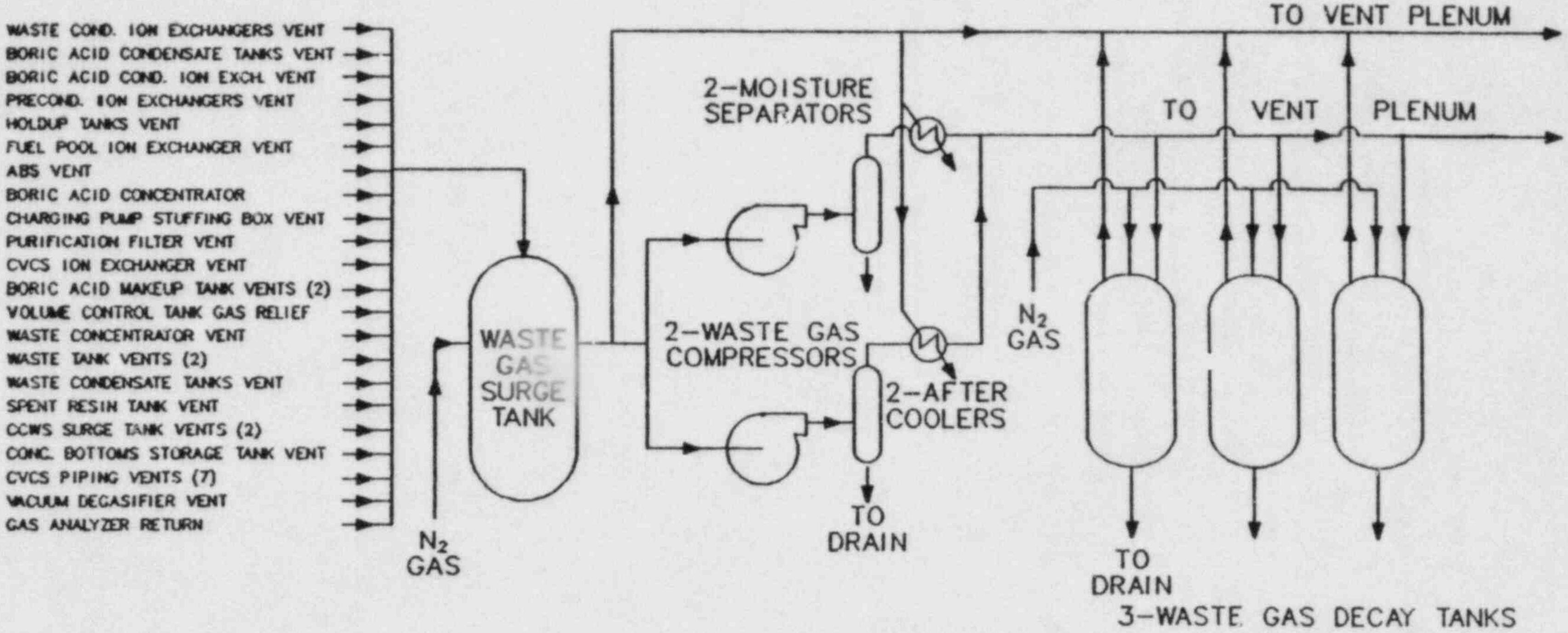


Figure 7. Schematic of Plant Number 3, Unit 2 Waste Gas System.

off at 2.5 psig. The second compressor starts at 7 psig and shuts off at 5 psig. At a WGST pressure of 0.5 psig, nitrogen gas is introduced to increase the system pressure to 2.5 psig.

To date, the Unit 2 WGS has not been used because of the small volume of waste gas required to be processed. There has been one directly discharged WGDT release (because there has only been one refueling outage). The reasons for lack of discharge are similar to the Unit 1 reasons. Neither WGS has ever had a fire. There are no known potential ignition sources.

Presently, the Unit 2 WGS is secured. A nitrogen cover gas is being maintained at ~2.5 psig in the WGDTs. Unit 2 has a multiple detector, on-line gas analyzer system that samples eleven locations. Seven locations (Loop A), which subject the gases to both hydrogen and oxygen analysis, are:

- Volume control tank
- Waste gas decay tanks (3)
- Waste gas surge tank
- Vacuum degasifier
- Containment vent.

The oxygen analyzer alarms at 3%. The other four locations (Loop B), which are routed only to a hydrogen analyzer, are:

- Holdup tanks (3)
- Spent resin tank.

3.4 Plant Number 4

This station has one operating nuclear power plant and two under construction. The operating unit, a Westinghouse unit which generates 456 MWe, began commercial operation in 1968. This plant has the only PWR WGS that has ever had a fire (July 1981). The WGS is designed as a Type D system (Figure 2) which incorporates a catalytic recombiner for oxygen removal and cryogenic adsorption for removing noble gases. However, it also has the compressors and waste gas decay tanks characteristic of a Type A system ahead of the recombiner cryogenic portion. Figure 8 shows a simplified block diagram of the overall WGS and Figure 9 shows the recombiner/cryogenic system. The main components of the WGS are:

- Gas collection header
- Waste gas surge tank
- Waste gas compressors (2)
- Gas decay tanks (3)
- Cryogenic/recombiner system.

The gas collection header receives inputs from:

- Flash tank
- Gas stripper
- Sampling station
- Reactor coolant drain tank
- Gas decay tank relief valves
- Nitrogen from the nitrogen header
- Relief valves and recirculation from the cryogenic unit.

The system uses nitrogen as a blanket and for purge. The surge tank (125 ft^3) is designed for 30 psig. Normal operation is 0.3 psig. The compressor operates automatically with one starting at 2.5 psig and shutting off at 1 psig. The other compressor starts at 3 psig and shuts off at 1.5 psig. The decay tanks, which are constructed of carbon steel, are filled to 100 psig. Maximum design pressure is 150 psig. The WGS is also constructed of carbon steel and is not designed to take explosion overpressures based on initial pressures of 100 psig.

The cryogenic system consists of:

- Liquid nitrogen tank (3398 gal)
- Filters

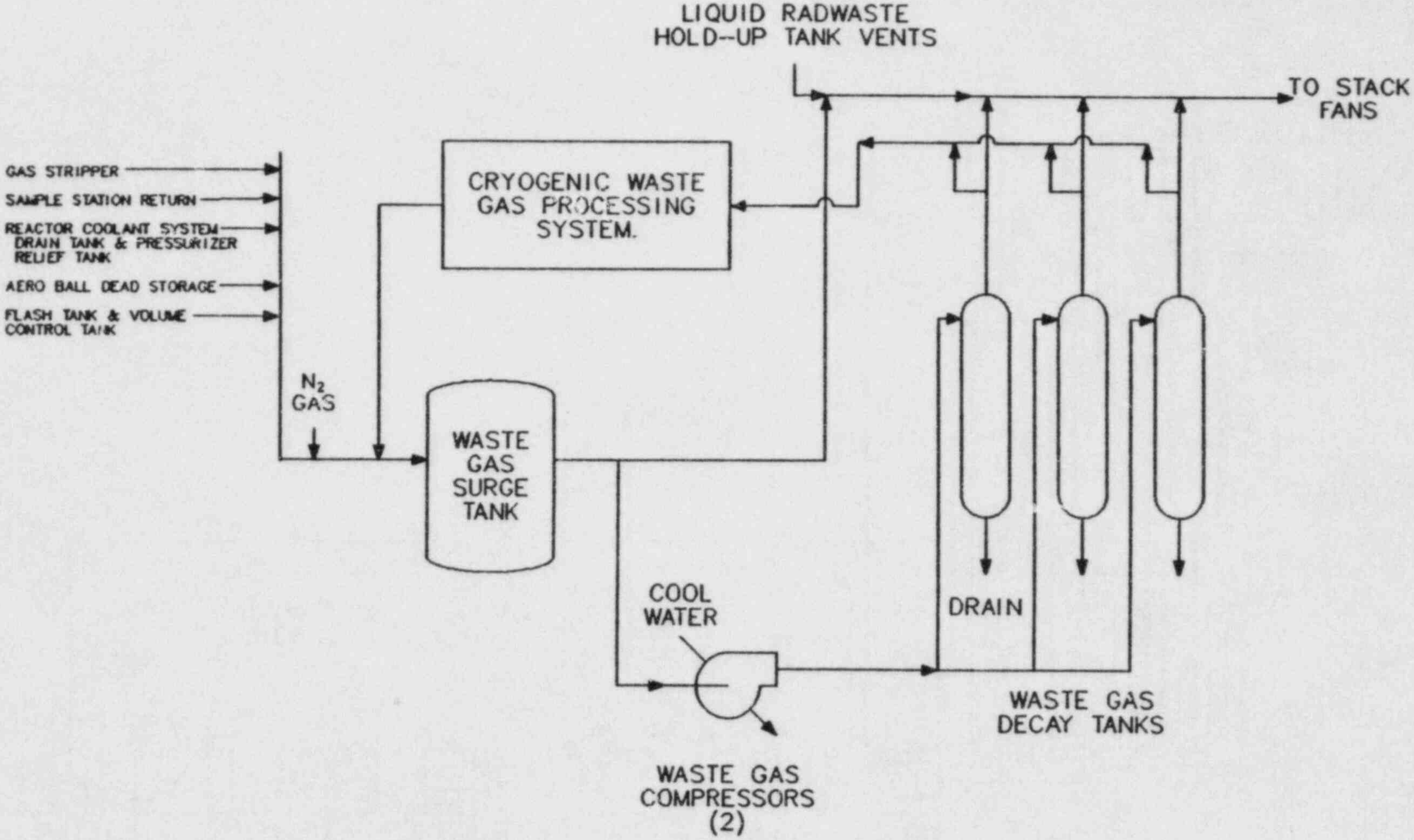


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Figure 8. Flow Schematic of Plant Number 4 Waste Gas System.

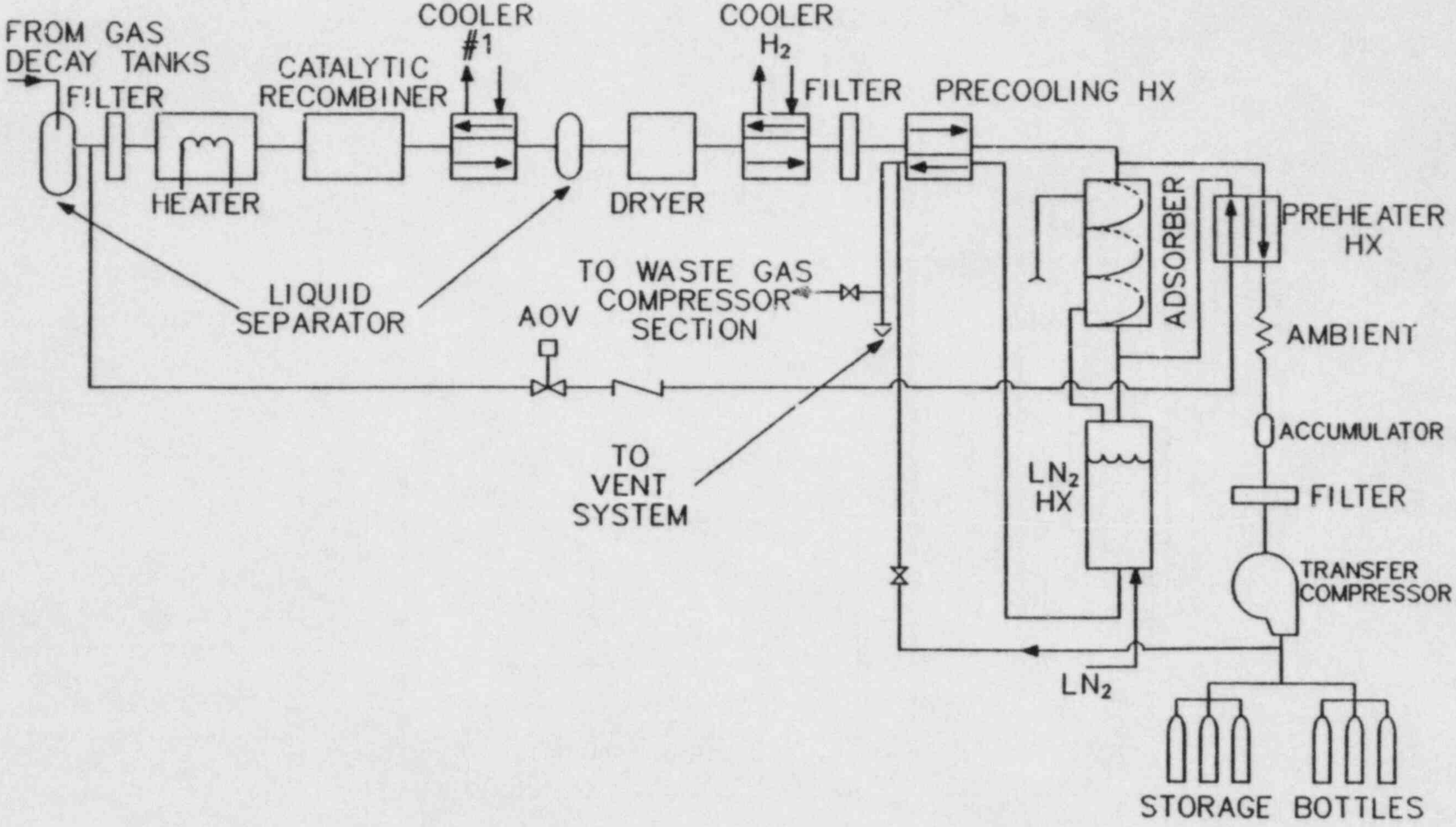

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Figure 9. Flow Schematic of Plant Number 4 Recombiner/Cryogenic Subsystem.

- Recombiner
- Liquid separators
- Drier
- Nitrogen pre-cooler
- Adsorber (charcoal)
- Accumulator
- Transfer compressor
- Six gas storage bottles.

The recombiner operates at 10 psig input and is sized to recombine up to 3% oxygen or 6% hydrogen. The charcoal adsorber (~1000 lbs) is cooled to -275°F (102°K) which is low enough to adsorb krypton and xenon but not hydrogen, oxygen, or nitrogen. Thus, the gas leaving the recombiner is primarily nitrogen which is exhausted to the vent system. At the time of charcoal regeneration, the adsorber is warmed and the released noble gases are pumped to storage bottles along with any nitrogen purge gas.

The system is maintained at positive pressure so all leakages are system outflows. There are basically three modes of operation:

- Direct discharge from the surge tank to the stack
- Compression of gases, then storage in the decay tanks followed by release
- Compression of gases to the decay tanks followed by recombiner/cryogenic processing of tank contents.

The third mode of operation was the one usually used up to the time of the July, 1981 fire. Since that time, the plant has not used the cryogenic/recombiner unit because of the damage to the recombiner caused by the fire. Mode 2 has been used since the fire. When the plant receives the replacement recombiner, it is planned to return to the Mode 3 operation.

This plant has no on-line gas analysis capability in the compressor-decay tank portion of the WGS. There is one on-line oxygen monitor associated with the recombiner/cryogenic unit. The monitor, located at the recombiner outlet, has a range of 0 to 3% oxygen. Off-line analysis is provided via grab samples analyzed using a laboratory gas chromatograph.

Sampling and a gas analysis of a decay tank is performed only at the time a release is scheduled. During normal operation, one to three tanks are released per week, however, this depends on the plant operating mode. The yearly release averages less than 80 tanks/year.

In July, 1981, a fire occurred in the WGS. It occurred during the initial stage of processing the contents of a decay tank through the recombiner/cryogenic unit. Popping noises in the recombiner section indicated local combustion occurring in this section. Before it could be valved out, the incoming gas was ignited, this propagated back to the WGDT being processed. The ignition was, therefore determined by the utility to be the recombiner. The direct cause of ignition was presumed to be a high oxygen concentration in the recombiner unit. The recombiner is designed to handle a maximum of 3% oxygen. Above this concentration, the recombiner temperature can become high enough to cause ignition. The cause of the high-oxygen concentration was traced to instrument air (normally maintained at 10 to 20 psig above the nitrogen system) that entered the nitrogen system at locations where the nitrogen serves as the backup gas to the instrument air. This occurred because the check valves isolating the two systems were not installed in accordance with the manufacturer's recommendations during Three Mile Island (TMI) backfit modifications. As a result, they failed to seal properly, thus providing a direct communication path between the two systems. The oxygen analyzer on the recombiner/cryogenic unit was inoperable. Its operability was not required by the operations procedure. The explosion caused damage mainly to the manway on the decay tank and to the recombiner. Although the system was designed as a Type D system, the actual operation when using the recombiner was a batch sequential process. That is, the WGS was operated as a Type A system (no recombiner in use) until one or more tanks were filled and needed to be emptied. The contents were then processed (only one WGDT at a time) through the recombiner/cryogenic part of the system. Since the recombiner was the actual ignition source, the probability of this high oxygen mixture igniting would have been reduced had the recombiner not been used, and the tank contents simply discharged as in a Type A system. Total release of activity from this event was a factor of ten below the maximum allowable due to the high dilution of the stack and meteorological factors. This ignition is the first fire known to have occurred in a PWR waste gas treatment system. The consequences, both radiological and to the plant equipment, were relatively minor.

It is of interest to note that:

- o Had the oxygen monitor at the recombiner been in operation, the fire might very well have been prevented
- o The likelihood of a fire under the combination of in-leakage of instrument air into the WGS would have been reduced had there been no recombiner
- o Use of on-line gas monitoring instrumentation in the compressor/WGDT section upstream of the recombiner/oxygen unit would have given advance warning of oxygen buildup and allowed control measures to be taken.

3.5 Plant Number 5

This is a two-unit plant, with each unit having 860 MWe Westinghouse 3-loop reactors. Units 1 and 2 began commercial operation in 1977 and 1980, respectively. The WGS was supplied through Westinghouse by Air Products and Chemicals Company. The WGS for each unit is of Type 3 (Figure 2c).

The WGS for each unit represents a new Westinghouse system designed for zero radioactive release over the 40 year design life of the plant. This design uses a recirculating system that also incorporates a redundant hydrogen recombiner to remove hydrogen. The radioactive gases are stored permanently in WGDTs. In practice, for reasons to be discussed below, no releases occur during operation, but some effluent is released during shutdown and startup for refueling outages. Both Units 1 and 2 have implemented the model RETS3

The WGS is a closed loop system incorporating two compressors, two hydrogen recombiners, and six waste gas decay tanks for normal power service and two gas decay tanks reserved for service at startup and shutdown. The major gas sources to the WGS are:

- VCT Gas Space
- Waste and Recycle Evaporation Stripping Column
- Reactor Coolant Drain Tank
- Recycle Holding Tanks.

The reactor coolant drain tank also acts as an additional header for other sources of input (e.g., holdup tanks exhaust, CVCS ion exchangers vents, etc.). Figure 10 is a simplified block diagram of the system. The hydrogen catalytic recombiner is normally on-line at all times during plant operation with the flow being about 40 to 50 cfm as it travels from the compressor to the recombiner to the active WGDT and back to the compressor. The bulk of the gas flow is nitrogen, with the main hydrogen and fission gas source coming from the VCT. System pressure is always positive at 1 to 2 psig at the compressor input. The system plumbing is carbon steel and there are no known external leaks. The WGS is not designed to withstand explosion overpressures.

There are two modes of operation, a low-pressure mode and a high-pressure mode. In the low-pressure mode, which is used for normal-power operation, flow is from the compressor to the recombiner to the in-service WGDT (operating pressure ~30 psig) and back to the compressor. The high-pressure mode is used for shutdown and startup operations. In this mode, valves are aligned so that flow is from the compressor to the WGDT (up to 100 psig) and then via the throttle valve to the recombiner. This allows buffer storage of the excess hydrogen removed during shutdown without exceeding the recombiner's capacity. In actual practice the system cannot be operated as a zero-release system. Some gas is released during startup after refueling. At this time there is insufficient hydrogen in the gas stream to recombine with the oxygen. The system design does not provide for controlled admission of additional hydrogen needed to complete recombustion of all the oxygen. Consequently when tanks are full they must release it.

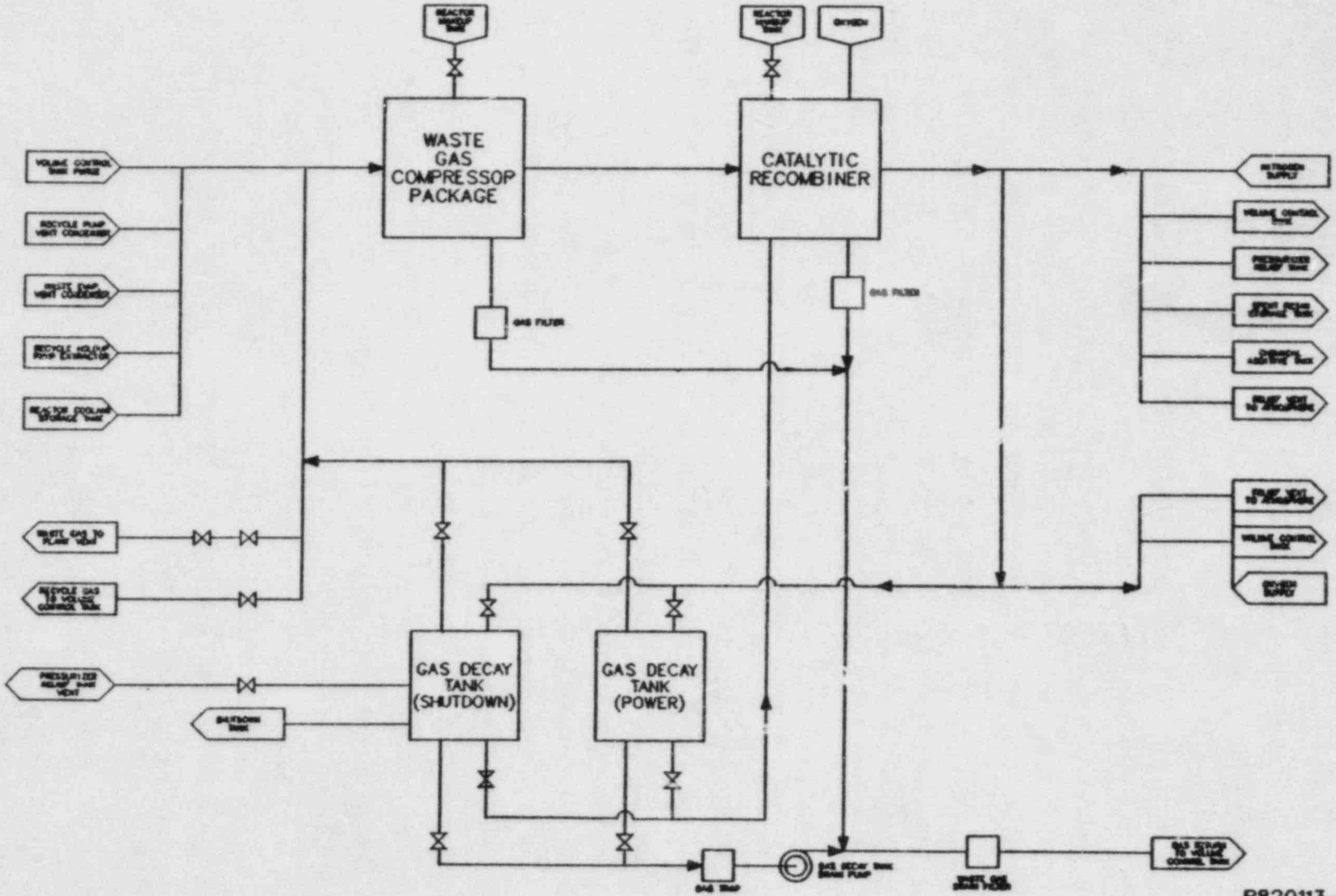

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Figure 10. Flow Schematic of Plant Number 5 Waste Gas System.

There are four on-line analyzers for each recombiner unit, two for hydrogen and two for oxygen. These analyzers monitor four different locations (Table 3). The recombiners are sized to handle 6% hydrogen normal, 9% maximum. Controlled oxygen (up to 3%) is added to recombine the hydrogen.

Unit 1 encountered some problems getting the recombiner system working properly. As a result, modifications were made. These modifications have also been incorporated into Unit 2. Moisture collection problems associated with oxygen analyzers have been corrected by relocating components and sloping lines properly. The auto-control valve that controls oxygen addition to the recombiner had too slow a response time and was replaced with a Moore Pneumatic Controller. Also, lines to the oxygen analyzers were shortened and a bypass was incorporated into the system so a continuously flowing sample is always available. As a result of these modifications, the system presently works the way it was designed. There are no plans to make any further modifications. Plant personnel did comment, however, that to make such a system truly a zero release system over the 40-year plant life, they would recommend installing a separate recombiner with controlled hydrogen addition to handle the high oxygen concentration that occurs during startup. They believe this would be safer than having a single recombiner (with both controlled oxygen and hydrogen addition available) to handle both the hydrogen-rich and oxygen-rich gases. No fires or detonations have occurred in the WGS of either unit. The only known potential ignition source is the recombiner.

As mentioned earlier, both Units 1 and 2 have implemented the model RETS. The 2% oxygen limit in the RETS means that this recombiner is operated below its design capacity (3% oxygen). Plant personnel believe the one-hour time limit for reducing oxygen from 4% to 2% is unrealistic. They have never encountered this situation, but believe it could easily require more than one hour to accomplish this reduction. Even then, all that could be done would be to release the effluent.

3.6 Plant Number 6

This is a four-unit plant, of which Units 3 and 4 are in construction. Units 1 and 2 are Westinghouse 3-loop designs. Unit 1 began commercial operation in 1978 and Unit 2 in 1980. The Architect/Engineer was Stone and Webster. Units 1 and 2 both produce 940 MWe power. They are served by a common WGS. This system is Type C (Figure 2), but incorporates compressors as well as a recombiner. However, the recombiner is bypassed and has never been used. The WGS operates entirely as a Type A system.

The WGS incorporates a gas stripper ahead of the waste gas compressor and recombiner system. Figure 11 shows a simplified block diagram of the WGS and Figure 12 shows the recombiner section.

The gas stripper strips gas from the primary coolant and liquid transferred from the primary coolant transfer tank. These are mixed with vents from the VCT and primary drains transfer tank. These are then compressed (two compressors) into the Gas Stripper Surge Tank. Gas from the stripper section is then compressed using waste gas compressors into the WGDTs. As designed, the WGS is a closed loop consisting of two waste gas compressors, two WGDTs, one catalytic recombiner, and connecting piping, valves, etc. The plant had difficulties even prior to plant initial startup in getting the recombiner to operate properly. They elected not to use it and it is permanently bypassed. This plant has not had a fire or detonation in their WGS. The only known potential ignition source is the recombiner which is permanently valved out and not used.

The WGS has on-line analyzers both in the compression section and in the recombiner section. The compression section analyzers (one hydrogen, one oxygen) are located on a recycle line between the decay tank outlet and the waste gas surge drum. The hydrogen analyzer has a 0 to 100% range and the oxygen analyzer has two ranges, 0 to 1% and 0 to 5%. The oxygen alarm is set at 2% on the higher range. In addition, there is an on-line oxygen analyzer on the gas stripper surge tank at 0 to 1%, and an alarm at 0.1%.

At the time of the survey, none of the on-line analyzers were in service. The problem was stated to be delay in getting replacement parts. The plant has also had difficulty in getting calibration gases for on-line analyzers that are in the proper composition range.

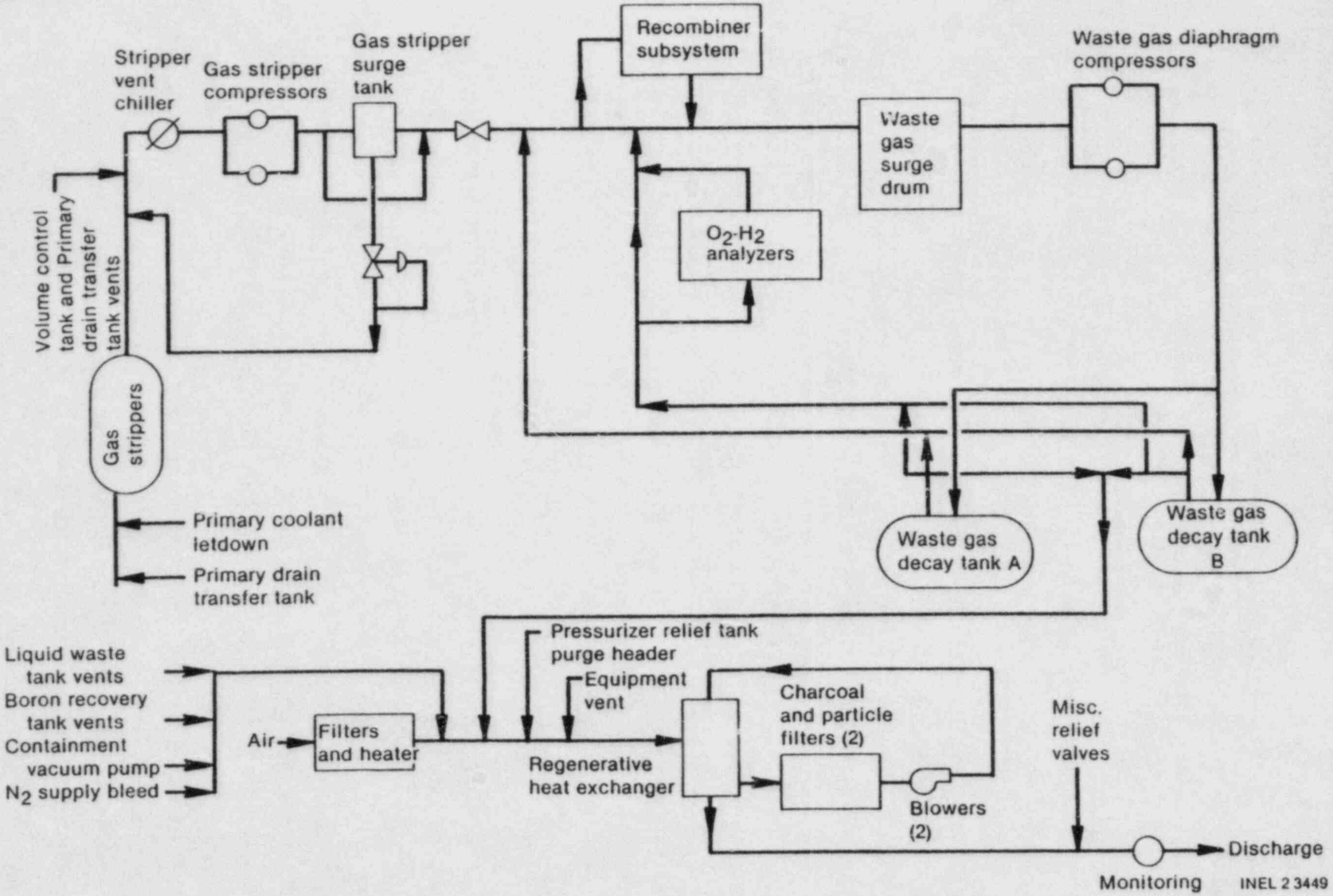

Figure 11. Flow Schematic of Plant Number 6 Waste Gas System.

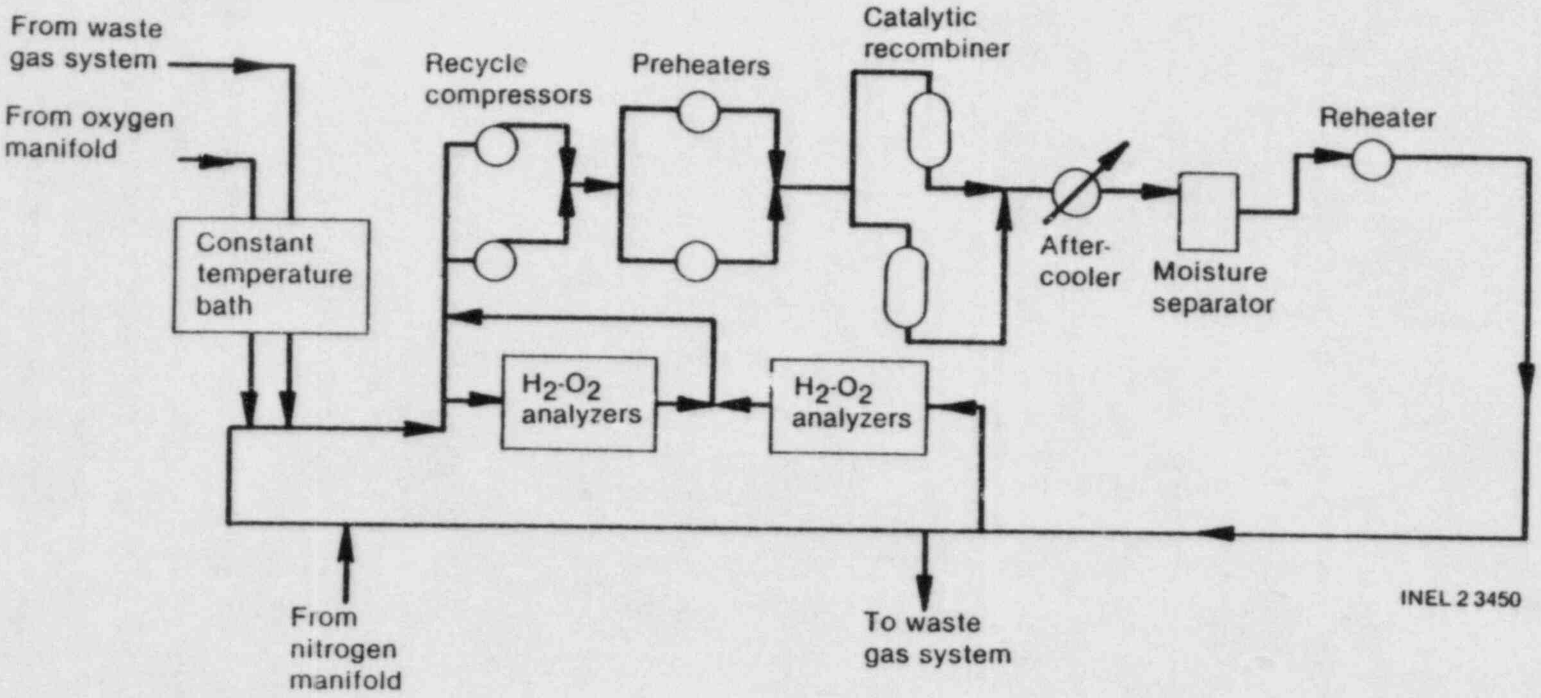

Figure 12. Flow Schematic of Plant Number 6 Recombiner Subsystem.

The plant had a total of 19 WGDT discharges during 1981. This period included a refueling shutdown for both units.

3.7 General Comments

3.7.1 Discussion

It has been noted earlier that the different plant operational modes can result in different concentrations of hydrogen and oxygen. How fast these concentrations change is not known, nor the extent to which there rates may vary among different plants. Such information cannot be determined at those plants which perform grab sampling and off-line analysis only on a waste gas tank and only at the time it is to be discharged. The time intervals between samples in such a case can range from a few hours (e.g., shortly after shutdown) to several weeks. This type of sporadic sampling schedule precludes any systematic knowledge of buildup of concentrations toward the flammable range. Thus for most plants using this type of sampling schedule, if asked whether their waste gas composition was in the explosive range, they would not actually know, although they might have a fair idea, based on experience of what to expect in their waste gas tanks.

For plants that have continuously operated on-line gas monitoring systems, this information is available to the operator and can provide a basis for control measures to reduce concentrations and serve to indicate the quality of gas being released.

3.7.2 Effectiveness of Control Measures

Of the plants surveyed, only Plant 5 has implemented the model RETS. The RETS require redundant on-line hydrogen and oxygen monitors, and control measures to prevent the occurence of flammable concentrations of gases. Its implementation precludes the formation of a potential hazard and is much more restrictive than the control measures at other plants surveyed. Some of these have on-line gas monitors, but none have control provisions intended to keep the waste gas below flammability limits at all times. Those plants with on-line gas monitoring however, are in a better position than those without it to take action to prevent accummulation of explosive mixtures. Plants without on-line gas monitoring that use only grab samples and laboratory analyses are in a poorer position to assess the buildup or approach to a flammable mixture and then to control it.

3.8 Summary of Survey Observations

3.8.1 Summary of Survey Observations on Plant Design

- Three of the six plants visited have Type A systems (1, 2, 3), two have Type C systems (5, 6), and one has a Type D system with compressed gas storage (4).

- Of the three that have recombiners, Plant Number 5 uses it routinely, Plant Number 4 had a fire and the recombiner is presently in-operative, and Plant Number 6 does not use it at all.

- None of the systems are specifically designed to withstand the overpressures of a hydrogen explosion.

- Of the six plants, two have WGS construction plumbing of stainless steel, three are of carbon steel, and one (Plant Number 3) has one WGS being retrofitted with stainless steel. The other WGS is of carbon steel.

- All plants are designed to operate at a positive pressure throughout the WGS so that any leaks are out of the system rather than allowing air in-leakage.

- The maximum pressures used for WGDT storage, range from 100 to 200 psig and the number of tanks range from two to eight.

- All plants have the capability to analyze oxygen, hydrogen, and nitrogen. All use gas chromatographs for off-line analysis.

- Four of the six plants have some form of on-line gas analysis capability. Three of these four had their instrumentation in service at the time of the plant visit. Plants 1 and 4 have no on-line analyzers in the compressor-WGDT section and sample just prior to WGDT discharge. Plants 3, 5, and 6 have on-line analyzers, and take grab samples as needed or at WGDT discharge. Plant Number 2 has on-line analyzers and takes grab samples once per week.

3.8.2 Summary of Observations on Plant Experience

- All plants visited have had at one time or another gas concentrations in the combustible range - but not routinely.
- No fire or explosion has ever occurred at a PWR in a Type A system whose sole treatment is gas compression and storage.
- There are no known potential ignition sources internal to Type A systems.
- The fire that occurred in Plant Number 4 (Type D system but with WGDTs) would have been much less likely without the internal ignition source provided by the recombiner in the cryogenic unit.
- The main problems observed in the waste gas systems studied seem primarily to arise from moisture and/or leaks. Moisture in carbon steel systems causes corrosion, eventual valve problems, and possible external leaks. In monitoring system plumbing, improperly located or sloped lines, or lines too long, can cause moisture collection resulting in systems that do not work correctly.
- Sampling only just prior to a WGDT discharge is unsatisfactory in that the onset of problem conditions (e.g., trends toward explosive mixtures and their initial occurrence) goes undetected. This may be particularly important in systems with known potential internal ignition sources (e.g., recombiners).

4. EVALUATION OF RISKS OF EXPLOSION IN WASTE GAS SYSTEMS

In this section, we present a simplified evaluation of risks associated with explosions in PWR WGSs, since a full Probabilistic Risk Assessment (PRA) is beyond the scope of the program. One difficulty in performing even a simple numerical PRA is a scarcity of WGS information upon which to base probabilities. There are essentially two available numerical facts on explosions in WGSs, one for BWRs and the other for PWRs:

- In the 100 BWR reactor operating years between 1971 and 1977, there were 29 explosions in BWR off-gas systems. In 1981 and 1982 there was only one burn with 24 operating units.
- In 241 PWR operating years between 1963 and 1982, there has been one explosion in a PWR waste gas system.

Thus the probability of explosion per reactor operating year is estimated as

$$P = \frac{29}{100} = 0.29 \qquad \text{BWR (1971 to 1977)}$$

$$P = \frac{1}{48} = 0.021 \qquad \text{BWR (1981 to 1982)}$$

$$P = \frac{1}{241} = 0.0041 \qquad \text{PWR}$$

This tells us that PWR WGSs exhibit less likelihood of explosion than BWR off-gas systems, and that fires in BWR systems have been significantly reduced in the last 5 years. However, these probability values do not help us to compare one PWR WGS with another one.

Nevertheless, using a simple analysis based on PRA principles, available information allows a limited classification of risks according to WGS type (configuration). As will be seen, however, we do not have sufficient information to make clear distinctions among risks for some of the WGS configurations. The basic formulation for risk assessment is given by

$$R_T = \sum_i P_i \; C_i \tag{1}$$

where

R_T = Risk associated with an event (accident)

P_i = Probability of occurrence of the event(s) leading to the total accident

C_i = Consequences of each event

The two major potential consequences are:

- Damage to plant equipment as a direct result of an explosion.
- Premature release of radioactive noble gases contained in the waste gas system.

Other effects which can result from the two major consequences are:

- Fire/explosion hazard and radiological hazard to plant personnel in the immediate vicinity at the time of the event.
- Post-explosion radiological and/or fire hazard to plant personnel involved in recovering from the event.
- Initiation of other plant fires by the initial explosion.
- Plant shutdown due to damage and/or release or violation of a Technical Specification.

Thus,

$$R_T = [P_1 \; C_1 + a \; P_2 \; C_2] \tag{2}$$

where

P_1 = Probability that an explosion occurs

C_1 = Plant damage due to the explosion

P_2 = Probability of release of radioactivity

C_2 = Radiologic exposure due to released activity

a = Conversion constant to ensure the same units in both terms

P_1: Assuming that an explosive mixture exists in a WGS, an ignition source is required for the event. These sources can be either external or internal. From the standpoint of various types of WGSs, the probability of an externally caused event (e.g., welding torch, system leaking into an inadequately ventilated space, etc.) is assumed independent of the system type. For an internal ignition source, we make the assumption that a system that has a known potential internal ignition source has an intrinsically higher P_1 than one that does not.

$$P_1 = P_{1i} + P_{1e} \qquad (3)$$

where

P_1 = Total probability of an explosion

P_{1i} = Probability of an internal ignition occurring

P_{1e} = Probability of an externally caused ignition occurring

C_1: The damage factor, C_1, depends on the overpressure generated by the explosion. For given concentrations of gases, this, in turn, depends upon both the initial storage pressure and the available chemical energy inventory, i.e., the moles of combustible gases present.

Thus,

$C_1 \propto$ pressure and inventory

Hence, WGSs with higher storage pressures can have higher inventories of combustible gases and, therefore, are assumed to to have greater potential damage consequences if an event takes place.

P_2: The probability of radioactivity release from an explosion is assumed to be $P_2 = 1$.

C_2: The radiologic consequence, C_2, is exposure which is proportional to the time dependent inventory of stored radioactive gases.

Thus, bigger inventories have potentially larger consequences. Detailed design and scenario specific analyses are required to distinguish C_2 for different WGS designs.

We, therefore, shall assume P_2C_2 is constant, independent of a particular system design. This essentially implies that the total radioactivity inventory in each type system is the same at the time of the event. We will not evaluate this term any further but write:

$$R = R_T - aP_2C_2 = P_1C_1 \tag{4}$$

The analysis then, is keyed to the probability ($R = P_1C_1$) of explosion and its damage consequences. Further, since we do not have numerical values available, we shall make reasonable assumptions about relative sizes of the factors P_1 and C_1 for various system design configurations.

Potential internal ignition sources include friction of moving parts, internal electrical sparks, and catalysts. The sources of frictional heat or sparks are pumps, valve motion, or improperly grounded equipment. All PWR systems studied use diaphragm or water-sealed vane compressors. The use of diaphragm pumps (rather than piston pumps) reduces the liklihood of a friction initiated fire, as does the use of a water seal in the vane type compressors. Thus these pumps do not appear to represent a significantly potential ignition source. Sparks generated from valve movement have caused a problem in BWRs at least once. Another potential ignition source is sparking from improperly grounded HEPA filters. This has actually occurred in BWR off-gas systems. Another source, which we believe to be a major potential internal ignition source, is the presence of a catalytic recombiner. This is also suggested by BWR experience. Essentially all BWRs use an off-gas system that incorporates a recombiner, and experience indicates that several explosions (9 of 29) were ignited by the recombiner or the catalyst dust.[1]

For our simplified, relative risk evaluation, we assigned the following values of P_1 and C_1 based on internal ignition sources and pressure/explosive mixture. We also assigned a value b to P_{1e} since it is additive to P_{1i}.

Recombiner Presence	P_{1i}	P_{ie}	Pressure/Explosive Gas Inventory	C_1
No	P_o	b	Low	C_L
Yes	P_1	b	High	C_H

where

$p_1 > p_o$

and

$C_H > C_L$

The probability, p_o, contains the effects of all internal sources other than a recombiner, while p_1 contains the recombiner in addition to the other sources. "High" means pressures above 1 atmosphere typical of compressed gas storage (e.g., 80-200 psig). "Low" means pressures between 1 to 2 atmosphere. We assigned a damage consequence, C_H, to the high-pressure case and C_L, which is less than C_H, for the low-pressure case.

There are only four different cases of explosion risk, R, obtained from these assignments. These are:

Case	Presence of Recombiner	Pressure/Explosive Gas Inventory	Explosion Risk R
1	No	Low	$(p_o+b)C_L$
2	No	High	$(p_o+b)C_H$
3	Yes	Low	$(p_1+b)C_L$
4	Yes	High	$(p_1+b)C_H$

Table 6 shows these risks for the various WGS designs (Figure 2) and variations among them. The configuration defining the WGS variant within the basic WGS type is given in the second column of Table 6.

We attempted to make a relative risk classification among the four cases. As will be seen, this can be done in only three of the four cases. We assigned a subscript to R for each case, i.e., R_1 is risk for Case 1, etc., and compared risks by subtracting one risk from the other and using the fact that $p_1 > p_o$ and $C_H > C_L$.

$$R_2 - R_1 = (p_o + b)(C_H - C_L) \tag{5}$$

since

$$C_H > C_L$$

then

$$R_2 > R_1$$

$$\begin{aligned} R_3 - R_2 &= (p_1 + b)\,C_L - (p_o + b)C_H \\ &= p_1C_L - p_oC_H - b(C_H - C_L) \end{aligned} \tag{6}$$

$$\begin{aligned} R_3 - R_1 &= (p_1 + b)C_L - (p_o + b)C_L \\ &= (p_1 - p_o)C_L \end{aligned} \tag{7}$$

So

$$R_3 > R_1$$

$$R_4 - R_3 = (p_1 + b)(C_H - C_L) \tag{8}$$

So

$$R_4 > R_3$$

$$\begin{aligned} R_4 - R_2 &= (p_1 + b)C_H - (p_o + b)C_H \\ &= (p_1 - p_o)C_H \end{aligned} \tag{9}$$

So

$$R_4 > R_2$$

TABLE 6. RELATIVE EXPLOSION RISK OF VARIOUS WASTE GAS SYSTEM CONFIGURATIONS

WGS Type	WGS Configuration	Potential Internal Ignition-device (Recombiner)	Total Explosion Probability (P_1)	Pressure/ Potential Combustible Gas Inventory	Damage Factor (C_1)	Explosion Risk (R)	Case
A	Compression and WGDT High Pressure Storage	No	$p_o + b$	High	C_H	$(p_o + b)C_H$	2
B-1	No Recombiner. No WGDTs, Straight Through Separation	No	$p_o + b$	Low	C_L	$(p_o + b)C_L$	1
B-2	Recombiner Ahead of Charcoal Adsorber, No WGDTs	Yes	$p_1 + b$	Low	C_L	$(p_1 + b)C_L$	3
C-1	Low Pressure WGDTs Downstream of Recombiner	Yes	$p_1 + b$	Low	C_L	$(p_1 + b)C_L$	3
C-2	High Pressure WGDTs Upstream of Recombiner	Yes	$p_1 + b$	High	C_H	$(p_1 + b)C_H$	4
D	No WGDTs, Once Through Recombiner and Stores Only Noble Gases	Yes	$p_1 + b$	Low	C_L	$(p_1 + b)C_L$	3

Summarizing this we have:

$R_4 > R_3$

$R_4 > R_2$

$R_3 > R_1$

$R_2 > R_1$

or

$R_4 > R_3 > R_1$

and

$R_4 > R_2 > R_1$

It follows then that of the four classifications, two of them (Cases 2 and 3) cannot have their risks distinguished without further information. In going from Case 2 to Case 3 (see Equation 2), the probability of explosion has increased by adding a recombiner but the explosion consequences are reduced by operating at lower storage pressure. At the same time, the risk of externally ignited explosions is reduced by decreasing the storage pressure. Even if it were assumed that in a PWR the risk of ignition from sources external to the WGS were zero (b = 0), a relation between p_1 and p_o, and C_H and C_L is still needed.

In Table 7 the information from Table 6 is ranked according to risk from the highest (1) to lowest (3). In addition, the WGS of the plants visited are placed in Table 7 by their WGS configuration (Column 4).

Most plants visited fall into the second risk rank, four of the five being systems of Type A. Plant Number 6 is classified as Type A because the recombiner is not used. If the recombiner were used, the plant would be classified as Type C1 or C2 depending on the mode of pressure operation. Plant Number 5 has two risk levels since it has a high- and low-pressure mode of operation. Plant Number 4 has a Type D system but with WGDTs and therefore, is classed as a C-2 system.

TABLE 7. RANKING OF WGS TYPES ACCORDING TO RISK OF COMBUSTIBLE GAS EXPLOSION

Rank of Risk	Case Number	Risk	WGS Type	Plant Surveyed and (WGS Type)
1	4	$(p_1 + b)C_H$	C-2	4(C-2), 5(C-2) 6(C-2 design)
2	3	$(p_1 + b)C_L$	B-2, C-1, D	5(C-1)
	2	$(p_o + b)C_H$	A	1, 2, 3, 6-(actual operation)
3	1	$(p_o + b)C_L$	B-1	

We conclude from Table 7 that waste gas systems having both a recombiner and high-pressure storage exhibit the highest comparative risk of explosion. A system with neither a recombiner nor high-pressure storage exhibits the least risk. It is interesting to note that Plant Number 4 is the only PWR that has ever had an explosion in a waste gas system, and this system type is one that is in the highest risk category in Table 7.

It is clear that if both hydrogen and oxygen concentrations are kept below their flammability limits (4 and 5% respectively, see Chapter 5) that a safe condition is always met regardless of the potential ignition sources. Although this may not always be practical in a nuclear power plant it is a good safety goal. It is also apparent that continuous on-line monitoring for both hydrogen and oxygen at those points in the system where concentrations of these gases can differ (e.g., in the WGDTs and the compressor outlet stream) provides the most timely information upon which to base control measures. It provides early warning of the onset of potentially hazardous conditions. For this application, redundant monitors are advisable so that an out-of-service monitor does not stop the information.

5. RECENT RESEARCH ON HYDROGEN FLAMMABILITY AND DETONATION

The main objective of this part of the program was to assemble available data on the effect of initial pressure on flammability limits for hydrogen/air mixtures. However, since the accident at TMI, a number of studies have been initiated to better understand and model the flammability, detonation behavior, and characteristics of hydrogen mixed with air, nitrogen and/or oxygen plus other species such as water vapor, carbon dioxide, and chemical suppressants. At TMI, hydrogen was produced during the accident and an ignition and subsequent pressure rise occurred. The Nuclear Regulatory Commission (NRC) is supporting the preparation of a manual on the subject of hydrogen to better inform designers and operators in the nuclear industry.[4] Recently, a workshop was held on the impact of hydrogen on water reactor safety.[5] In addition, three major programs are in progress that address various aspects of the properties and chemistry of hydrogen. These programs are supported by NRC, the Electric Power Research Institute (EPRI), and the nuclear industry under the corporate auspices of the Atomic Industrial Forum (AIF) through the Industry Degraded Core Rulemaking (IDCOR) program. The NRC program, managed by Sandia Laboratories, is concerned with hydrogen production, transport, combustion, and control.[6] The EPRI program is investigating hydrogen combustion including ignition, and control with water fog and spray.[7,8] The IDCOR program, managed by the Technology for Energy Corporation, includes studies on hydrogen production, combustion, monitoring instrumentation, pre-inerting, suppression, and control.[9] The results from most of these studies should shortly begin to become available. In this section, we shall review the available data on the effect of initial pressure on flammability limits for hydrogen/air mixtures and discuss recently available theoretical, experimental, and modeling information on flammability and detonability, including limits of hydrogen/air or hydrogen/oxygen/nitrogen mixtures.

5.1 Hydrogen Flammability and Flammability Limits

Experiments to determine the lower flammability limit of hydrogen in hydrogen/air mixtures at ambient temperatures and pressures consistently indicate a difference in value between upward and downward flame propagation of 4% versus 9% respectively.[10,11] For safety purposes, flammability maps or diagrams of mixture compositions have been constructed to delineate the flammable regions from the non-flammable regions. The generally acceptable flammability diagrams for hydrogen/air/nitrogen mixtures and hydrogen/oxygen/nitrogen mixtures are given in Figures 13 and 14, respectively. Note that the lower flammability limit differs for upward and downward propagation in both instances. The upper flammability limit for hydrogen/oxygen mixtures is 95%/5% while for hydrogen/air mixtures, it is 75%/25%. Assuming air is ~20% oxygen (actual is 21%), then 5% of the 25% air at the upper flammability limit is oxygen. In both hydrogen/oxygen and hydrogen/air mixtures, a minimum of 5% oxygen must be present to sustain combustion (flame propagation). Note from Figure 13 that one simple way of controlling flammable hydrogen/air mixtures is through addition of sufficient excess nitrogen. A tank or system containing 71% excess nitrogen will dilute any flammable hydrogen/air mixture and render the mixture nonflammable (i.e., the resulting hydrogen/air/nitrogen mixture lies outside the flammable envelope).

The minimum spark ignition energies necessary to initiate hydrogen/air mixtures are given in Figure 15 for the pressure range 0.2 to 1.0 atmosphere.[12,13] For stoichiometric hydrogen/air mixtures (~30% hydrogen) at 1 atmosphere, 20 microjoules (20×10^{-6} joules) is sufficient to initiate the hydrogen/air mixture. This represents an extremely small quantity of energy and illustrates how easily stoichiometric hydrogen/air mixtures can be initiated. For hydrogen/air mixtures with compositions of 10%/90% and 55%/45%, ~150 microjoules (0.15 millijoules) of energy is sufficient to initiate the mixtures. As pressures are increased above 1 atmosphere, the minimum ignition energy necessary to initiate hydrogen/air mixtures should decrease to even lower values.

The effect of initial pressure on the flammability limits of hydrogen/air mixtures has not been extensively studied. For most materials, the lower flammability limit decreases, and the upper flammability limit increases as initial pressures are increased from 1 atmosphere (760 torr). Thus, the flammable range widens as the initial pressure is increased. However, for some fuels, this is not the case. Narrowing of the flammability

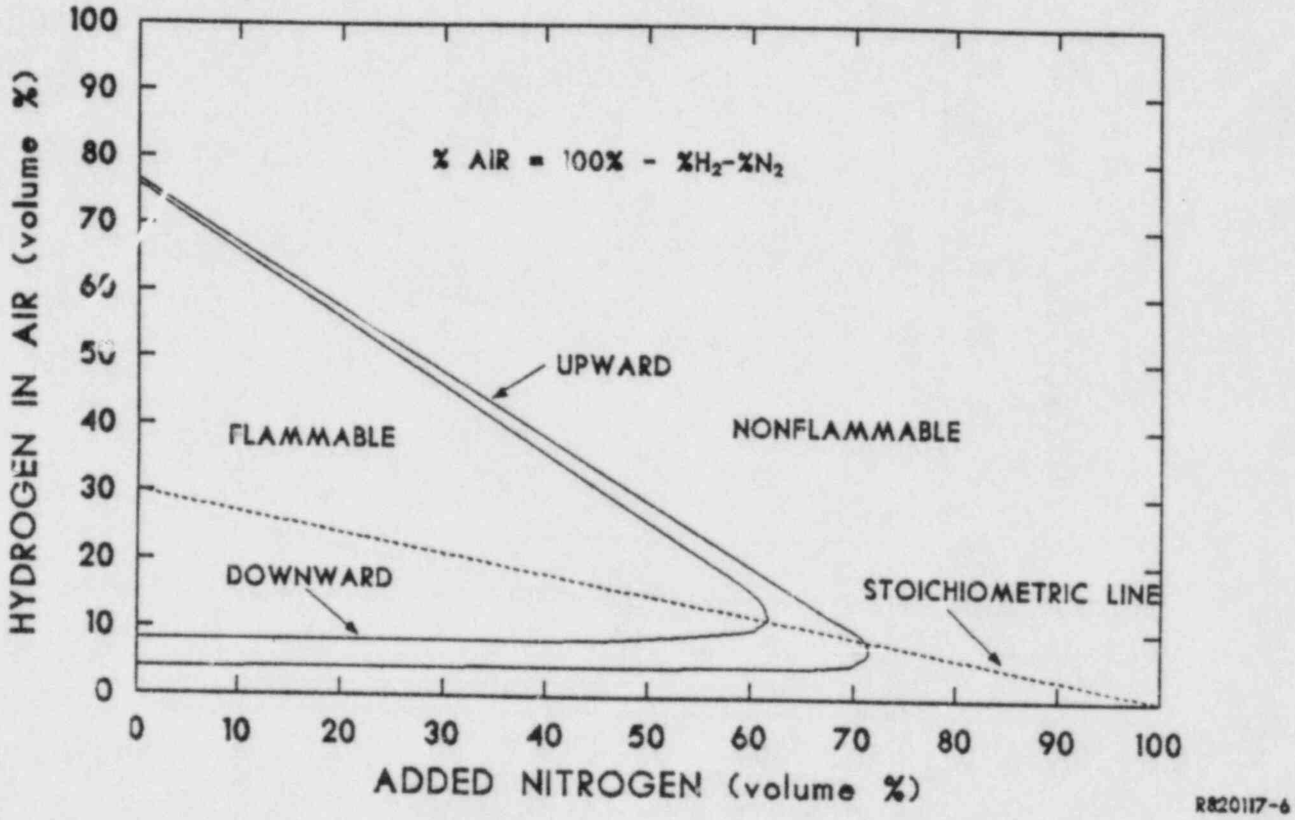

Figure 13. Flammability Map for Upward and Downward Flame Propagation in Hydrogen/Air/Nitrogen Mixtures.

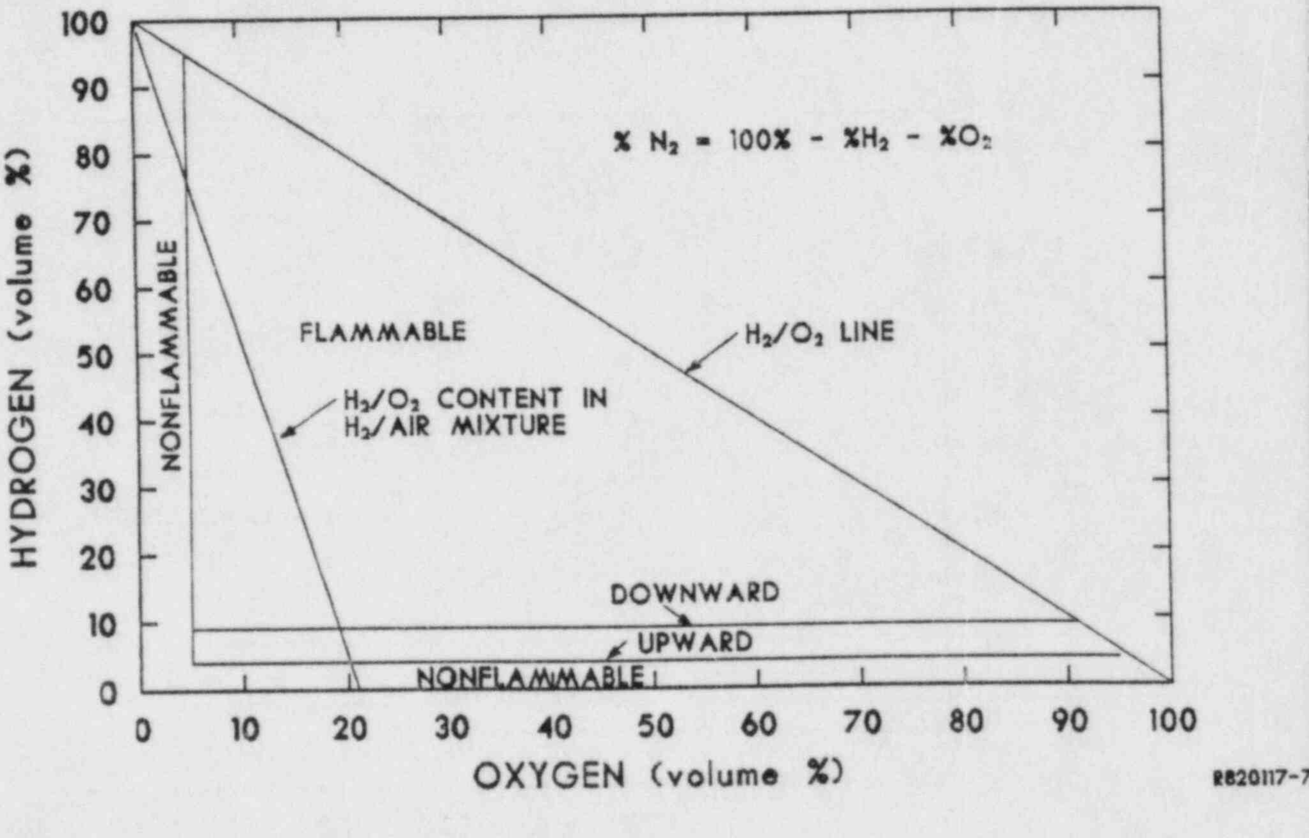

Figure 14. Flammability Map for Upward and Downward Flame Propagation in Hydrogen/Oxygen/Nitrogen Mixtures.

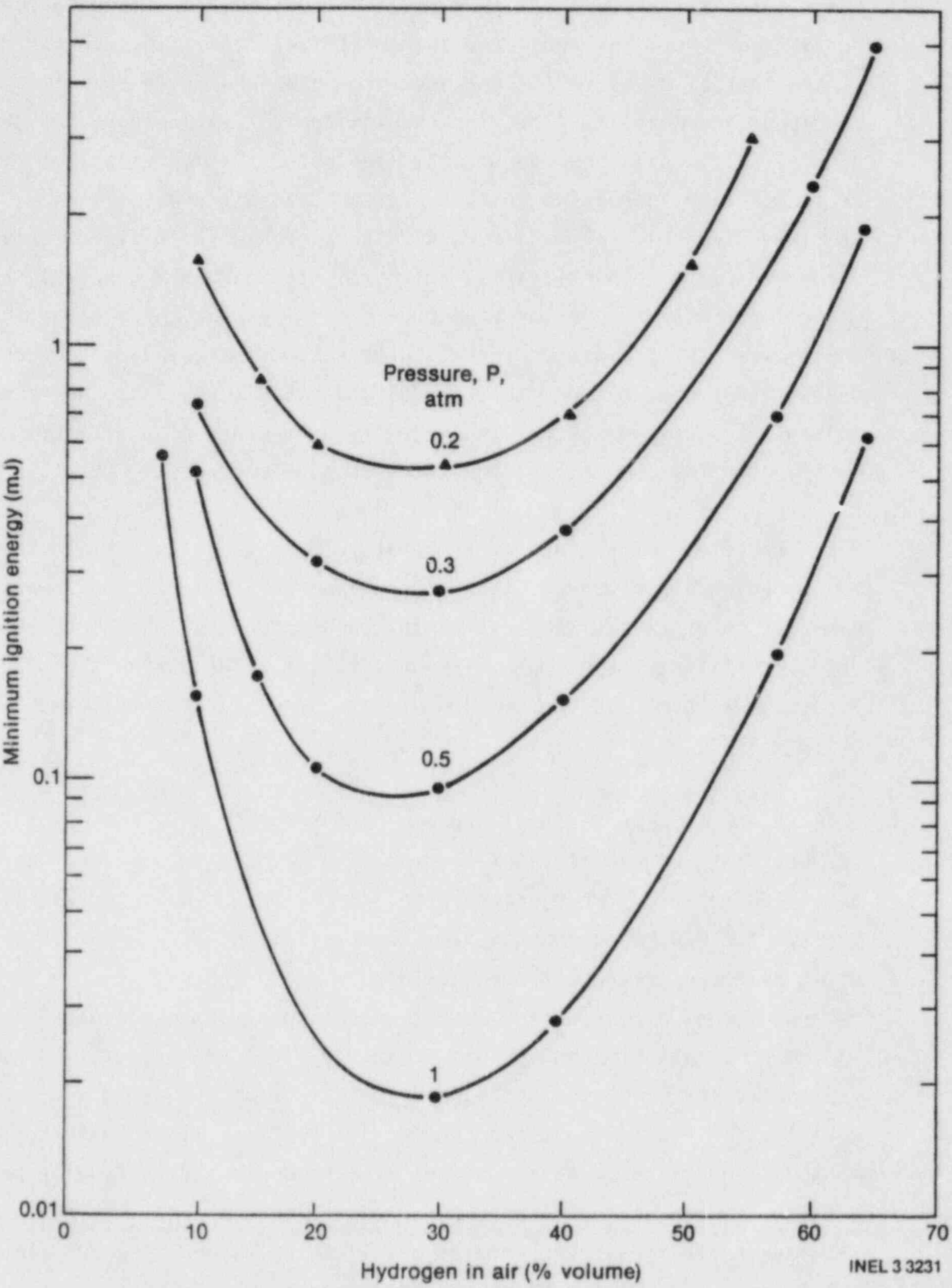

Figure 15. Spark Ignition Energies for Hydrogen/Air Mixtures.

limits has been observed for hydrogen/air, carbon monoxide/air, and paraffin hydrocarbon/air mixtures.[10] Figure 16 gives the available data for the behavior of the upper and lower flammability limits of hydrogen/air mixtures as the initial pressure is increased from atmospheric to 200 atmospheres.[10] The lower flammability limit increases with initial pressure to 20 atmospheres (~300 psi), then decreases. The upper flammability limit initially decreases with increasing initial pressure, then increases. Thus, it appears that the flammable range narrows with an increase in initial pressure above atmospheric. At higher initial pressures (10 to 20 atmospheres), the flammable range widens. To our knowledge, this apparent behavior of the flammability limits for hydrogen/air mixtures has not been validated. What is needed is an examination, theoretical and experimental, of the effect of initial pressure on the burning velocity, the order of the reaction(s) contributing to combustion, and the quenching processes.

The effect of increasing temperature does not show anomalous behavior for hydrogen/air mixtures. The lower flammability limit for downward propagation decreases linearly as the temperature is increased from 20 to 400°C. Similarly, the upper flammability limit for downward propagation increases linearly as the temperature is increased from 20 to 400°C[10] (Figure 17).

Recently, computational and modeling efforts and a review of the current state of knowledge of flammability limits and pressure development have been reported for hydrogen/oxygen/nitrogen and hydrogen/air mixtures.[14,15] In the computational study, a flammability diagram for premixed hydrogen/oxygen/nitrogen mixtures was constructed using a time dependent, one-dimensional numerical model that couples chemical reactions, including a full kinetics scheme; thermophysical properties; and hydrodynamic transport, including the non-linear convection of the fluid.[14] Two methods were initially tried to determine the flammability limit. In the first method, a decision is made for each mixture whether the flame is propagating. In the second method, the trend of several runs of the same fuel to oxidizer ratio is used to predict the limiting value. The computational model solves a time dependent set of coupled conservation equations in

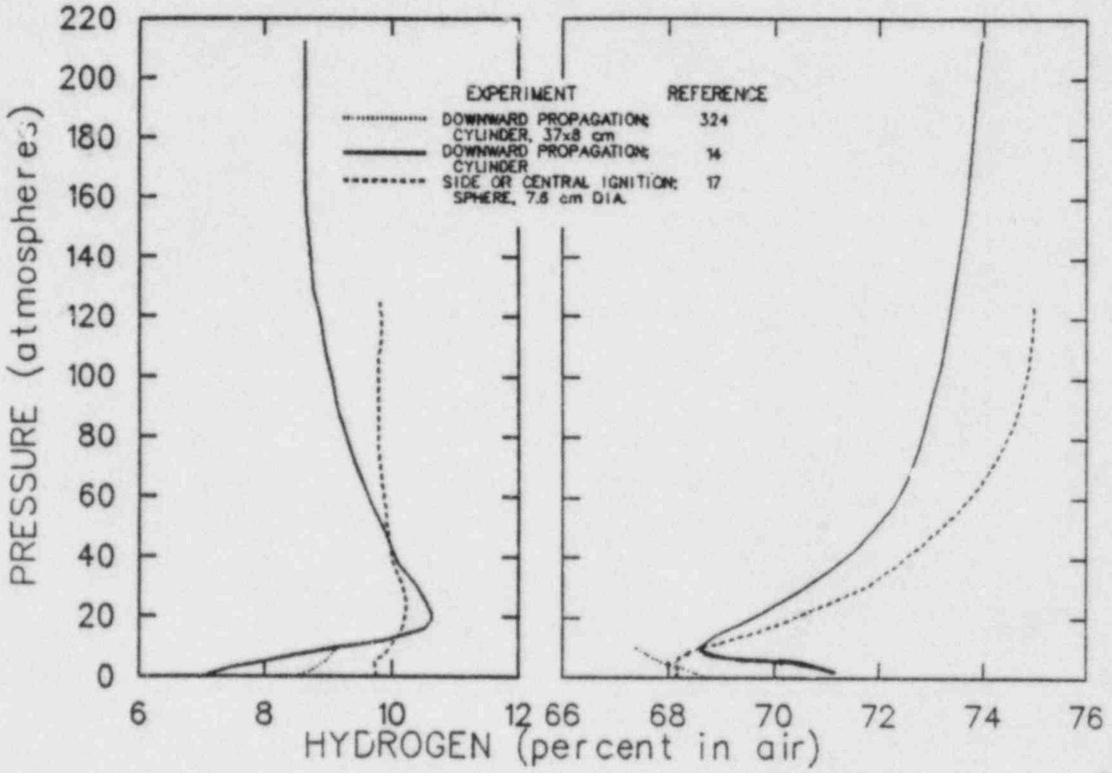

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Figure 16. Effect of Initial Pressure on Flammability Limits of Hydrogen/Air Mixtures.

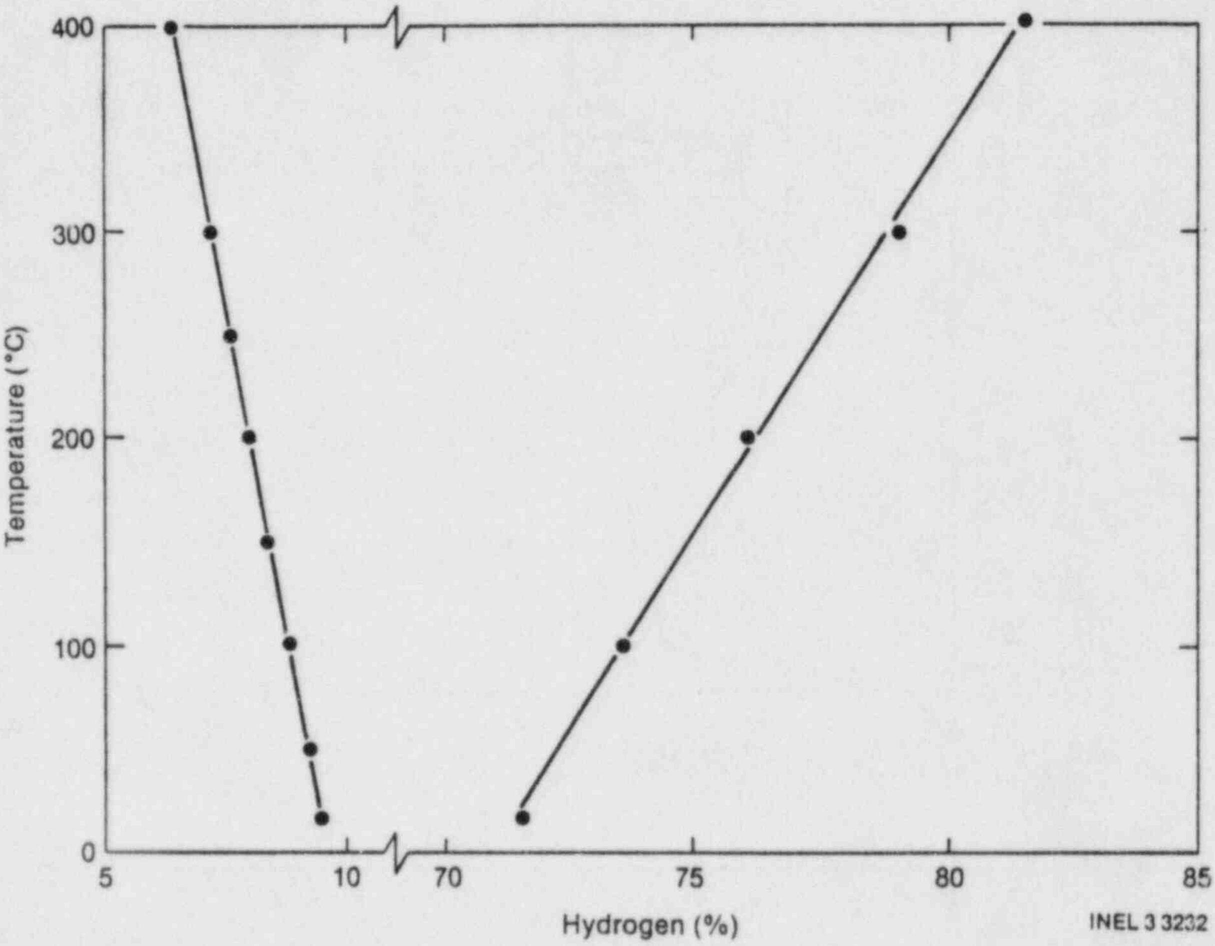

Figure 17. Effect of Temperature on Downward Propagation Limits of Flammability of Hydrogen in Air.

one-dimension for total mass, momentum, and energy as well as individual species densities. The method of solution for these equations uses the technique of asymptotic timestep splitting.[14,15] With this technique, individual processes, represented by equations, are solved separately through a series of algorithms, then asymptotically coupled together. A literature study was used to develop the final rate scheme of 58 chemical reactions. The model requires, as input data, initial concentrations of chemical species with corresponding masses and enthalpies, the reaction scheme with rate constants, the binary diffusion coefficients, and the molecular collision cross-sections.

The flammability limit diagram deduced from the computational model is given in Figure 18. The criterion finally used to determine flammability was the following: a stable flame was produced if the rate of chemical energy release exceeded the thermal relaxation of the initial input energy. The stars in Figure 18 represent flame propagation, and the open squares represent non-flammable mixtures. The top diagonal line in the figure represents hydrogen/oxygen mixtures and the lower diagonal line is the possible oxygen content based on hydrogen/air mixtures. The "X"s represent experimental flammability limit data taken from the literature. The upper flammability limit agreement between experiment and calculation for hydrogen/oxygen and hydrogen/air is quite good. However, agreement of the lower flammability limits between experiment and calculation is not as good. The calculated lower flammability limit value is higher than the experimental one in both cases (hydrogen/oxygen and hydrogen/air). Considerations of flame speed, a measure of net reaction velocity, as well as the present criterion used for flame propagation may be necessary. More work needs to be performed near the lower limit in order to achieve better agreement between experiment and the computational model.

The review of flammability behavior, including flammability limits, in hydrogen/air mixtures proposes a simple theoretical model to describe a complex set of fluid dynamical interactions.[15] A number of non-adiabatic processes are proposed that compete with flame propagation and dissipate energy (power) from the combustion wave. The five non-adiabatic processes that quench propagation at a finite limit velocity are identified as:

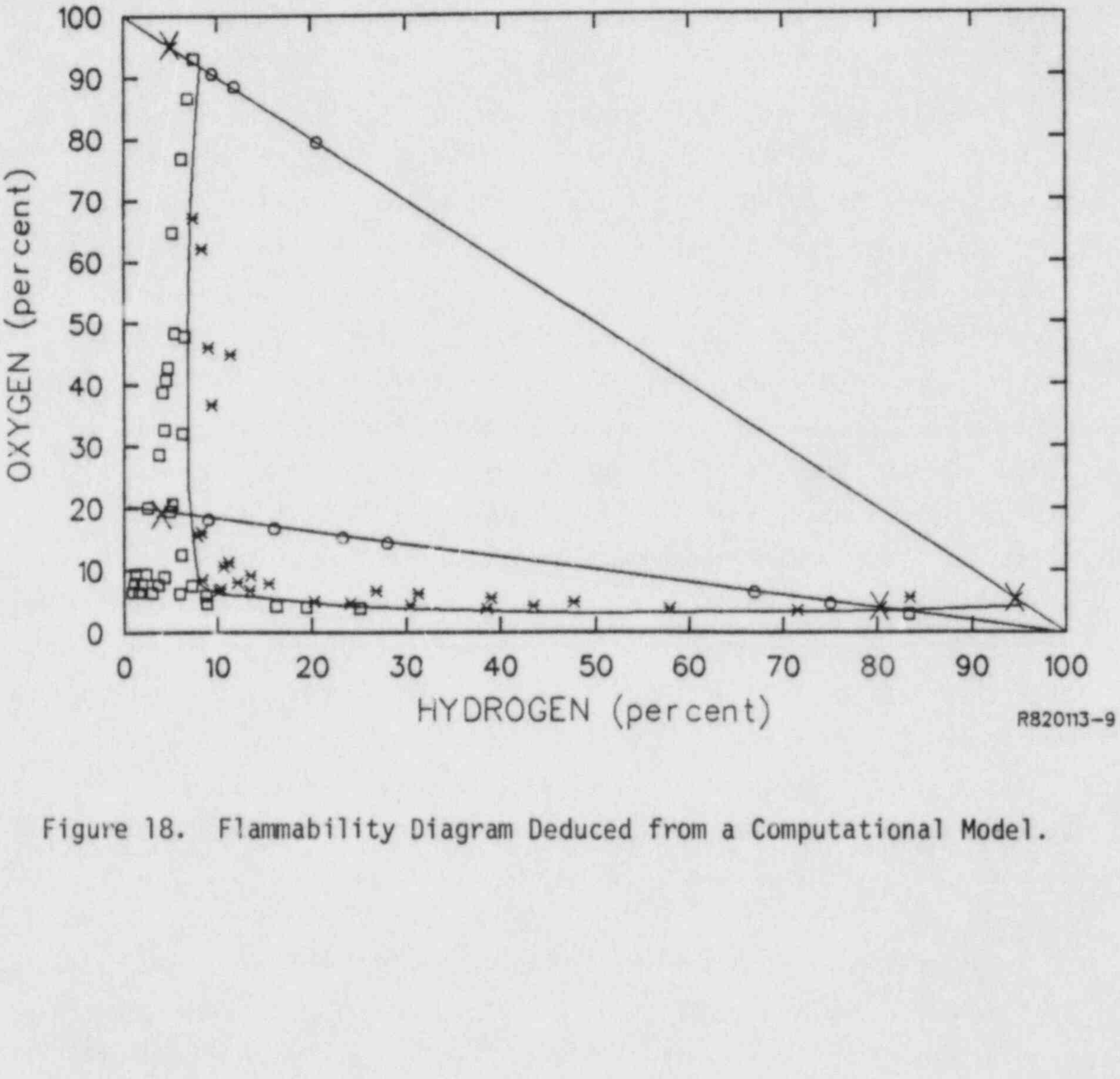

Figure 18. Flammability Diagram Deduced from a Computational Model.

- Free buoyant convection
- Conductive-convective wall losses
- Radiative losses
- Selective diffusional demixing
- Flame stretch or flow gradient losses.

Upward and downward flame propagation in near limit mixtures exhibit differences in both the flame and flow structure. It is observed, during upward flame propagation in tubes, that the flame front curvature, which is spherical, remains even during quenching of the flame. During downward propagation in tubes, the curvature diminishes and the flame front is flat at extinction. These observations can be qualitatively explained. An initially spherical flame kernel with a uniform, upward buoyant acceleration vector, normal to the flame front, accelerates the upward propagation vector. The net effect of this buoyancy is to maintain curvature as the spherical flame kernel expands and rises. For downward propagation, the buoyant acceleration vector is directed opposite to the outward normal propagation vector at the flame front. Thus, buoyancy decelerates propagation in the lower segment of the flame kernel. The net effect for downward propagation is to reduce curvature and generate a flattening as the flame kernel expands. Buoyancy is the process responsible for the existence of flammability limits as they are conventionally measured.[15]

One other process, selective diffusional demixing, exerts a major influence on the flammability behavior of lean hydrogen/air mixtures. This process, coupled with hydrogen's high diffusivity, distinguishes hydrogen from other fuels. Hydrogen's higher molecular diffusivity gives it a strong tendency to generate cellular flames or curved flamelets during flame propagation. This phenomenon also occurs in fuel-rich heavy hydrocarbon/air mixtures. The process of selective diffusional demixing causes the combustion wave to act as though it were richer or leaner than its initial composition, depending on whether the fuel or the oxidizer molecule has the higher diffusivity.

Flammability limits are influenced by the selective diffusion process. As described above, buoyancy forces influence flame front curvature with upward propagation maintaining curvature and downward propagation reducing curvature (tendency to flatten the front). However, in downward propagation, curved cells are generated by selective diffusional demixing independently of buoyancy while in upward propagation, buoyancy and selective diffusion work together to enhance flame front curvature. Figure 19, taken from Reference 15, illustrates the gaps or differences in flammability limits between upward and downward flame propagation for air mixtures of methane, ethane, pentane and hydrogen. An unusual composition scale was chosen for the abscissa. A lean fuel composition is expressed as an oxygen dilution ratio which is the ratio of oxygen actually present to that required for complete conversion of the fuel to CO_2 and H_2O. The fuel dilution ratio, representing rich fuel compositions, is the ratio of fuel actually present to that required for complete conversion of the oxygen present to CO_2 and H_2O. For example, a mixture of 15% methane and 17.8% oxygen is fuel rich. Complete conversion of 17.8% oxygen to CO_2 and H_2O requires 8.9% methane. The fuel dilution ratio is $\frac{15}{8.9} = 1.7$.

Note from Figure 19 that the large differences between the upward and downward flammability limits occur in the fuel-rich regions of the heavy hydrocarbons and in the fuel-lean region for hydrogen. These large differences in composition between the upward and downward flammability limits occur in the composition regimes where cellular flames are stable. In hydrogen, the upward propagating combustion wave acts as if it were richer than its initial composition because selective preferential diffusion enriches the flame front. Thus, upward propagation is possible at leaner initial compositions than downward propagation, and the gap appears between the two lean limits. In summary, "the large gap in hydrogen is caused by the fact that the hydrogen molecule has a much higher molecular diffusivity than the oxygen molecule, which causes the selective diffusional enrichment of the flame front in hydrogen, generating cellular flames, whose curvature is further enhanced by buoyancy, which further enriches the flame front in hydrogen."[15]

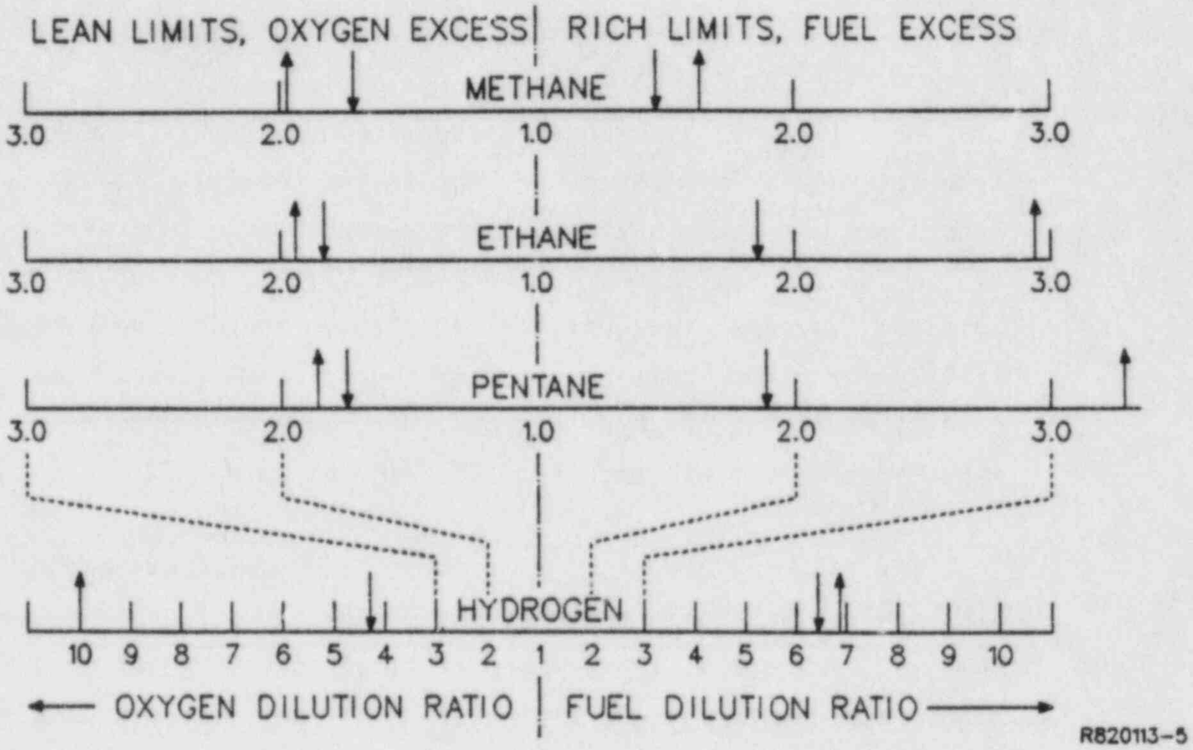

Figure 19. Effect of Cooperative Enhancement of Buoyancy-Induced Flame Curvature and Selective Diffusional Demixing on Flammability Limits.

We include here a brief comment on turbulence as it affects the pressure rise from combusting hydrogen/air mixtures with 4 to 8% hydrogen compositions.[15] Turbulence causes the propagation to be more isotropic, and reduces the limitations of buoyancy, the time available for radiative losses, and the asymmetries responsible for convective wall losses. It also restricts the role of selective diffusion. The sum total of these effects is that, in this composition regime (4 to 8% hydrogen), turbulent propagation generates a greater pressure rise than laminar propagation for the same initial hydrogen/air composition. This is illustrated in Figure 20.

5.2 Hydrogen Detonability and Detonation Limits

We review in this section information recently presented on hydrogen/air detonations.[17] This reference reports the results of both small scale laboratory and large scale tests to measure and attempt a unified correlation of the fundamental detonation parameters (i.e., detonation cell diameter, critical tube diameter, critical initiation energy, and detonability limits) for direct initiation of hydrogen/air mixtures. The lower/upper detonation limits for hydrogen concentrations in hydrogen/air mixtures have reported values that range from 18.2%/58.9% to 13%/70%.

The reported correlation of detonation parameters begins with the empirical relationship noted by Mitrofanov and Soloukhin between detonation cell size (diameter) (λ) and the critical tube diameter (d_c) for low pressure oxygen/acetylene mixtures.[17,18] They observed that

$$d_c \cong 13\lambda, \text{ circular tube} \qquad (10)$$

$$d_c \cong 10\lambda, \text{ two dimensional channel} \qquad (11)$$

where the critical tube diameter, d_c, is the smallest diameter which will support a stable detonation. The correlation, $d_c \cong 13\lambda$, has since been validated by a number of other investigators working at higher pressures and with other fuel systems.[17]

"This important correlation between a dynamic detonation parameter (i.e., the critical tube diameter) and a fundamental quantity that

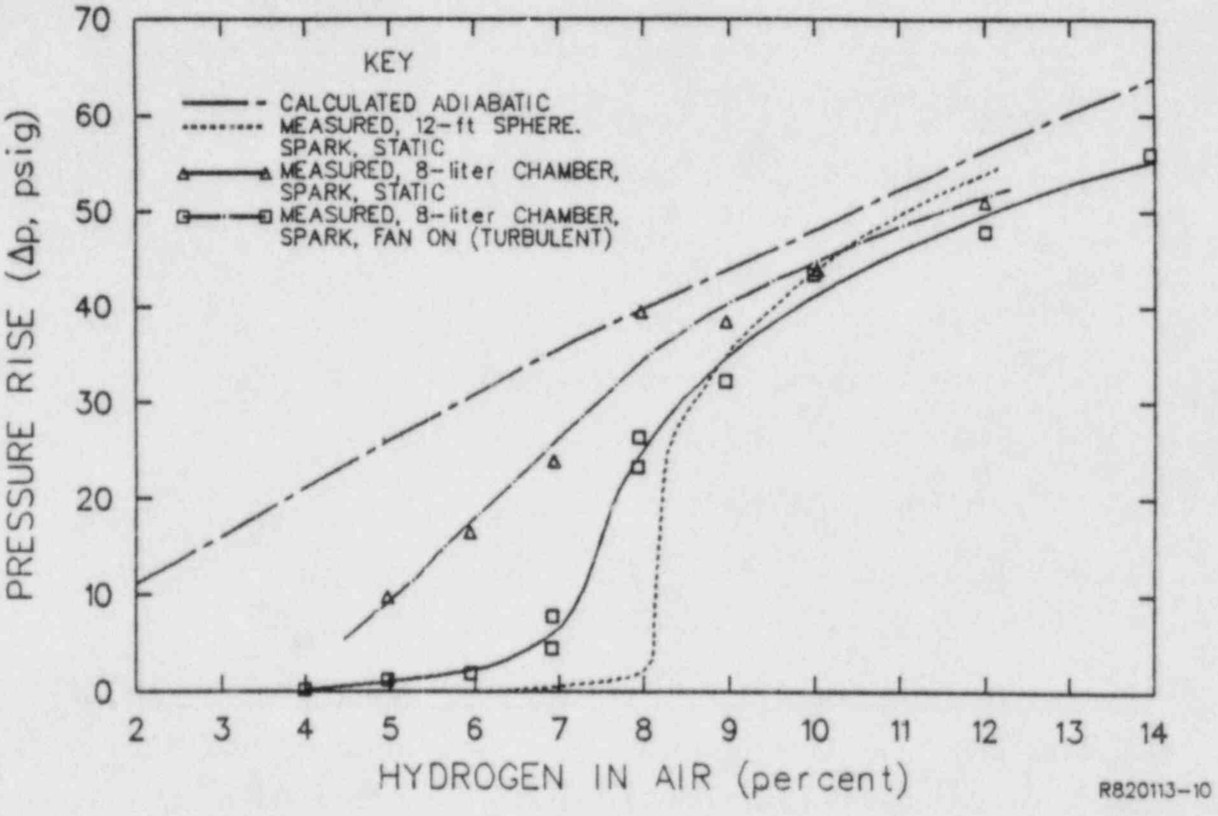

Figure 20. Comparison of Pressure Rises from Turbulent and Static Combustion of Hydrogen/Air Mixtures.

characterizes the chemical length scale of the detonation itself, now provides the stepping stone towards a unified correlation between the other "dynamic" detonation parameters, such as the initiation blast energy and detonation limits, with the cell size."[17]

To relate the critical tube diameter to the initiation energy, the authors argue that the critical tube diameter characterizes a minimum surface energy required for the transformation of a planar wave to a spherical wave. When a blast has decayed to the Chapman-Jouguet strength in the case of blast initiation by a concentrated charge, the total surface energy of the wave should be at least equal to the minimum surface energy required for planar to spherical wave transformation.[19] Equality of surface energy yields the relationship

$$4\pi(R_s^*)^2 = \frac{\pi d_c^{\,2}}{4} \qquad (12)$$

where

R_s^* = blast wave surface radius when $M_S = M_{CJ}$

M_s = Mach number of the spherical wave

M_{CJ} = Mach number of the Chapman-Jouguet wave

This leads to the relationship

$$R_s^* = \frac{d_c}{4} \qquad (13)$$

From the strong blast decay law for spherical detonations, Equation (13) and Equation (10), a direct relationship is obtained between critical initiation energy (blast energy or charge weight) (E_c), the detonation cell size (λ), and the critical tube diameter (d_c), as

$$E_C = 4\pi\gamma_o p_o M_{CJ}^2 I \left(\frac{d_c}{4}\right)^3 = \frac{2197}{16}\pi\gamma_o p_o M_{CJ}^2 I\lambda^3 \qquad (14)$$

where

γ_o = specific heat of initial gas mixture

p_o = initial pressure

I = energy integral (a calculated quantity) hydrogen) with a minimum cell size of 1.5 cm occurring between 29 and 30% hydrogen (stoichiometry = 29.6% hydrogen). The detonation cell data obtained from a number of different types of experiments is given in Figure 21. The cell size is also related to the induction length (L_i) by:

$$\lambda = A\, L_i \qquad (15)$$

where

A = constant

L_i = induction length

The induction length (L_i) is the thickness between the shock front and the equilibrium region in the burnt gas behind it. The induction length can be derived from

$$L_i = (D-U)\tau \qquad (16)$$

where

D = Chapman-Jouguet detonation velocity

U = burnt gas velocity

τ = induction time

Equation 15 is also plotted in Figure 21 for hydrogen/air compositions. Note the qualitative agreement. The authors indicate the need for further theoretical modeling. Conversion of the detonation cell size data, λ, to critical tube diameter data, d_c, via Equation (10) allowed data from critical tube experiments to be compared with the cell size data. Good agreement between the two sets of data was observed.

Note from Figure 21 that the detonation cell size (thus, the critical tube diameter) exhibits slower increases in value for changing hydrogen rich mixtures compared with changing hydrogen lean mixtures. This means that a detonation hazard can be sustained over a wider mixture range for hydrogen rich mixtures compared with hydrogen lean mixtures.

The detonation cell size data has been used to calculate the critical initiation energy (charge weight of tetryl) using Equation (14). The results are shown in Figure 22 along with the charge weights of tetryl, reported

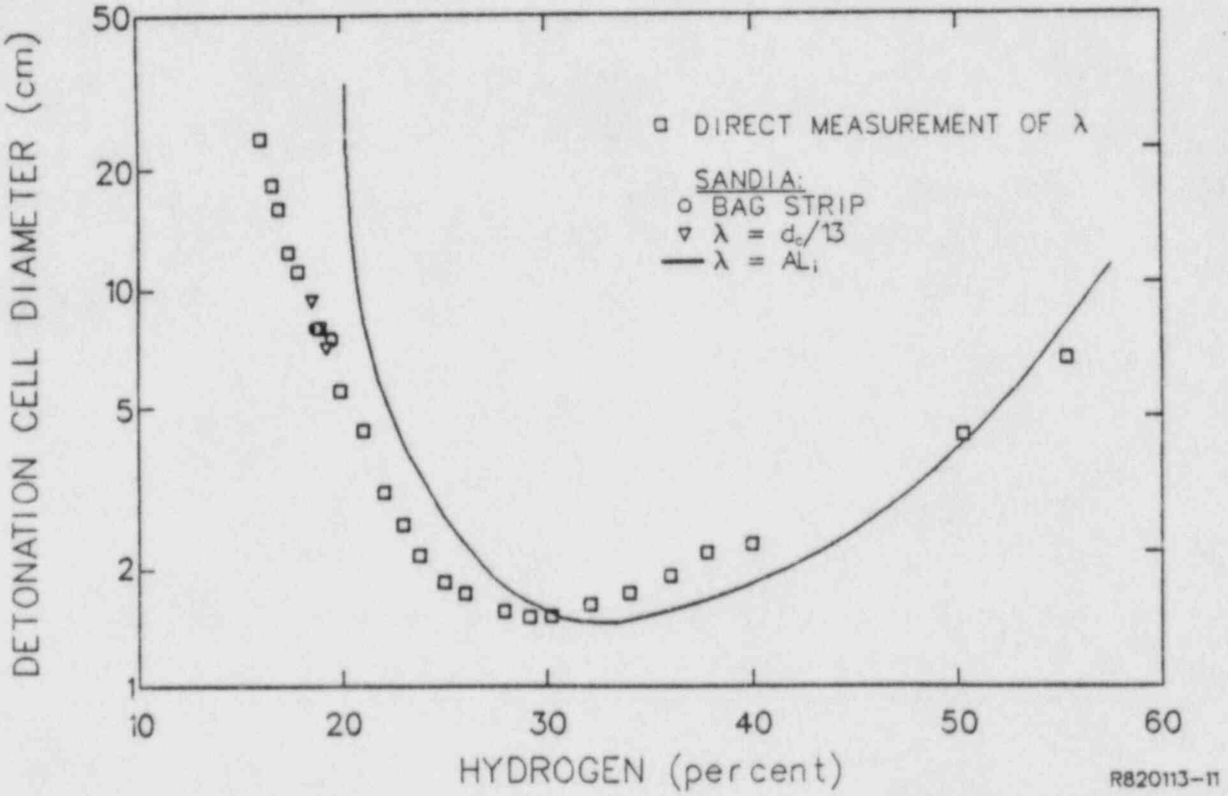

Figure 21. Detonation Cell Diameter as a Function of Hydrogen/Air Composition.

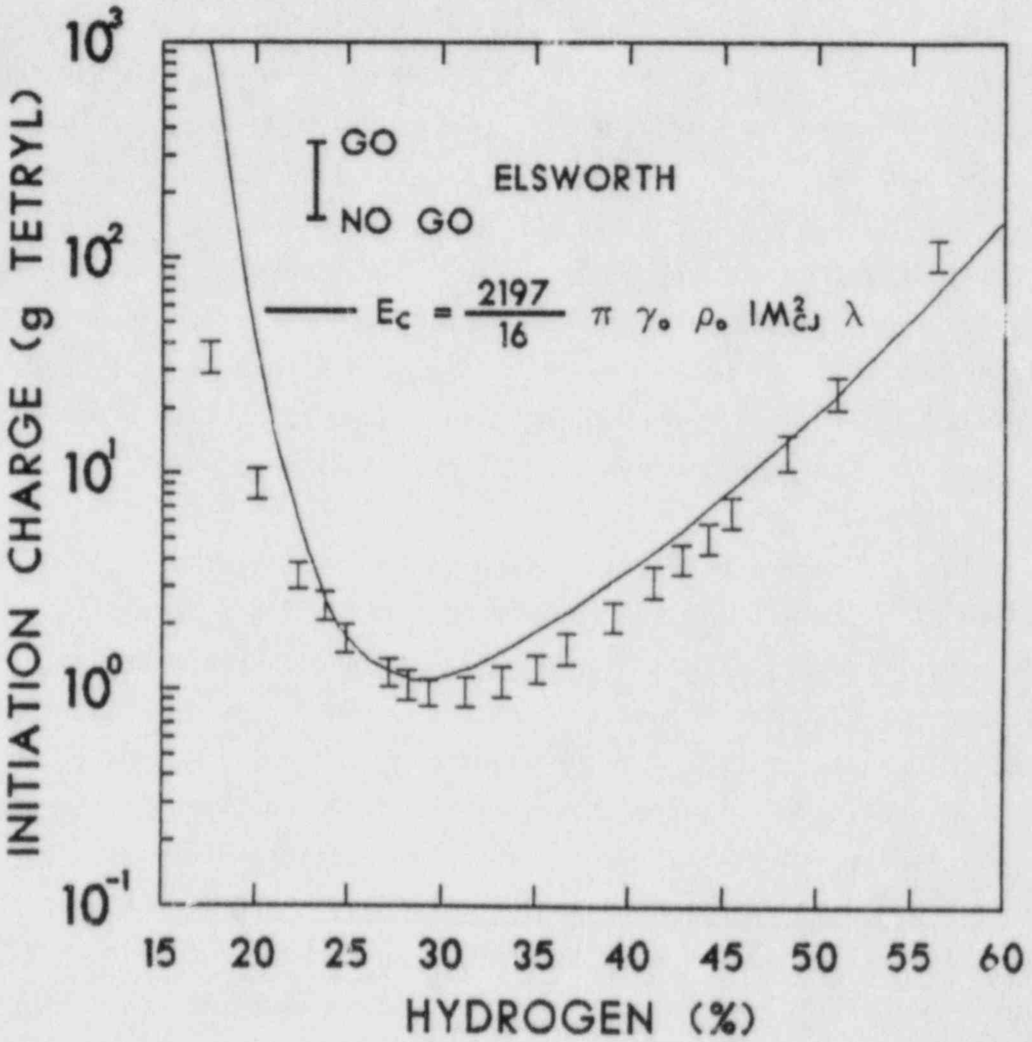

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Figure 22. Initiation Charge as a Function of Hydrogen/Air Composition.

by Elsworth, to initiate hydrogen/air mixtures.[17] Note the good qualitative agreement. However, for off-stoichiometric mixtures, the simple model deviates from Elsworth's data. Further experimental and/or theoretical work on the off-stoichiometric mixtures appears warranted. For the stoichiometric hydrogen/air mixture (29.6% hydrogen), Equation (14) predicts 1.15 grams of tetryl (5.0 kilojoules) as the minimum initiation charge (energy) compared with the 1.1 grams (4.7 kilojoules) reported by Elsworth. Detonation limits for hydrogen/air mixtures can now be selected from Figure 22 based on the equivalent charge of tetryl that is specified. For example, using Figure 22, lower/upper detonation limits of 18%/59% hydrogen are deduced for the direct initiation of unconfined hydrogen/air mixtures by 100 grams of tetryl (430 kilojoules).

Based on detonation cell size data, estimation of the detonation limits for hydrogen/air mixtures can be made for fully confined tubes, partially confined and unconfined clouds.[17] This is more fully discussed in the reference. Thus, the detonation hazard associated with a variety of geometries and hydrogen/air compositions can now be assessed.

We include here a brief discussion on recent investigations of the influence of obstacles and confinement on propogating flames.[20-23] Using a series of orifice plates with equimolar acetylene/oxygen mixtures, Knystautas, et al., determined that the requirement for deflagration to detonation transition (DDT) by turbulent mixing are (a) generation of large scale eddies of unburned gases in the turbulent wake of the obstacle, (b) sufficiently intense fine scale turbulence to promote mixing of hot combustion products entrained in the large eddies, and (c) generation of gradient fields inside the eddy to produce shock wave amplification.[20] For DDT to occur, the size of the large eddies must be at least of the order of the size of the detonation cell for any particular fuel/air mixture (for hydrogen/air mixtures, see Figure 22 for the appropriate detonation cell sizes).

In a series of companion studies, the influence of the presence of repeated obstacles on a freely propagating stoichiometric methane/air flame was examined.[21,22] Over a distance of 120 cm, flame speeds in excess of 400 m/s and overpressures of 9.3 psi were observed. Without the obstacles, the maximum flame speed was 9 m/s and no acceleration was observed over the last 20 cm of propagation. Modeling of the observed flame acceleration is based on a feedback coupling between the propagating flame and the flow field ahead of the flame. The series of obstacles used produced large scale flame folding which increased the rate of burning, yielded stronger flow field gradients, and produced the fine scale turbulence that also increased the burning rate. Data was also obtained on the effect of the ratio of obstacle height to obstacle separation distance.

Recently, the influence of the degree of confinement on observed flame acceleration due to the presence of repeated objects was reported.[23] It was found that confinement plays an important role in determining the strength (intensity) of the positive feedback mechanism that is responsible for accelerating the flame. Once venting destroys the ability of the mean displacement flow velocity to increase, the positive feedback mechanism becomes ineffective. Extension of these results to hydrogen/air environments should be made through a series of scaled obstacle experiments and/or analytical evaluations of appropriate accident scenarios.

6. HYDROGEN AND OXYGEN MONITORING INSTRUMENTATION

This section discusses the techniques and compares the operating characteristics of commercially available hydrogen and oxygen monitoring instrumentation. Although some instrumentation may not be appropriate for direct on-line use, they are included for information. The tables that list available instruments are structured so that additions can be made as new sources are found or new instrumental techniques are developed. As indicated in Section 3 and the data in Table 4 GC is used as the off-line instrument of choice in all the nuclear plants visited. The GC is a highly developed, reliable research and process monitoring analytical technique and it is not our intention to specifically discuss the technique of GC in this report. The GCs used in the six PWR nuclear plants visited use molecular sieve columns and thermal conductivity detection.

6.1 Hydrogen Monitoring Instrumentation

At least two studies of hydrogen monitoring instrumentation have recently been performed for the Nuclear Regulatory Commission (NRC).[24,25] We include, in this section, the relevant information on hydrogen monitoring instrumentation from those reports. Reference 24 identifies five commercially available classes of proof tested hydrogen monitoring instrumentation:

- Combustion
- Solid State
- Electrochemical
- Thermal Conductivity
- Absorption

There are a number of sub-classes of solid state instruments. These subclasses include diffusion controlled, adsorption-desorption controlled, room temperature, thin film, palladium gate MOS transistor, Schottky diode, and kryptonated solid detectors. In addition, a number of experimental techniques (instruments) for hydrogen detection were identified including ion current, acoustic, and fluidic devices. A brief discussion of each technique, taken from Reference 24, is given below. Characteristics and sources of commercially available instruments are given in Appendix A. Two instrument sources not listed in Reference 24 have been added to the table in Appendix A.

6.1.1 Combustion Detectors

The sensing element of a combustion detector is a hot wire or catalytic resistance element which is arranged as one arm of a Wheatstone bridge. The change in resistance of the sensing element, which is the basic quantity measured, is induced via the heat released during combustion that is initiated by heat from the hot wire or by catalysis. These detectors require the presence of oxygen or air so that combustion can occur.

The hot wire type of element is susceptible to burnout. The catalytic type, which operates at a lower temperature, can sustain a higher temperature rise without failure. Thus, the catalytic type can sense higher hydrogen concentrations (up to 7%) than the hot wire type.

Since this type of sensor generally responds to any combustible mixture, specificity is usually poor unless it is maintained by selecting the proper catalyst and calibrating with hydrogen.

6.1.2 Solid State Detectors

A number of sub-classes of solid state detectors (SSDs) have been identified. These are discussed separately below.

6.1.2.1 Diffusion Controlled SSD. This solid state sensor, tailored for hydrogen specificity, use a semiconductor material fabricated from a metal oxide-silica type material with embedded collector and platinum wire heater. The heater determines the operating temperature which is maintained below the boiling point of water. The sensor is affected by moisture concentrations exceeding 10% by volume.

Diffusion of hydrogen into the semiconductor lowers the resistance between collector and heater. This detector senses to 8% hydrogen as well in the low parts per million (ppm) range.

6.1.2.2 Adsorption-Desorption Controlled SSD. This sensor, mainly stannic-oxide (SnO_2), is fabricated from a sintered semiconductor material on a ceramic tube. A heater coil is located in the center of the tube. The resistance of the sensor changes with gaseous adsorption and desorption on the material surface. Sensitivity varies with heater voltage, ambient temperature, and humidity. Specificity can be poor although a hydrogen monitor calibrated to detect up to 10% hydrogen is commercially available.

6.1.2.3 Ambient Temperature SSD. This sensor, which is fabricated from carbon granules in plastic, is unheated, and operates at ambient temperature, and also responds to surface adsorption. Since resistance measurements are used for the detection of heavy hydrocarbons and current measurements are used in the detection of hydrogen and light hydrocarbons, specificity is poor. The sensor is temperature and pressure sensitive.

6.1.2.4 Thin Film SSD. One configuration of this sensor is a three-layer structure fabricated as a film of palladium deposited over a film of SnO_2 on a refractory chip. A resistance heater maintains operating temperature between 100 and 200°C. The device appears to operate in such a fashion that the change in conductivity (resistance) across the semiconductor film is proportional to hydrogen concentration.

6.1.2.5 Palladium Gate MOS Transistor SSD. This sensor is fabricated as a palladium metal gate deposited on a metal oxide semiconductor (MOS) substrate. The voltage drop across the transistor, arising from the dipole layer at the palladium-metal oxide interface which changes the threshold voltage, is proportional to hydrogen concentration. This device, which has been used in gas mixtures containing less than 1% hydrogen, is temperature sensitive and is not specific to hydrogen when contaminant and non-hydrogen chemical reactions occur on the palladium surface.

6.1.2.6 Schottky Diode SSD. A Schottky diode sensor has been fabricated from both palladium-cadmium sulfide (CdS) and palladium-titanium oxide (TiO_2). The decreased threshold voltage at the palladium-metal oxide or sulfide interface is related to the hydrogen concentration. In the hydrogen concentration range of 0.05 to 0.5%, the palladium-CdS detector is slow to reach equilibrium (10 to 15 minutes at 298 to 323°K). The palladium-TiO_2 detector is insensitive to other gases unless heated to 1000°C.

6.1.2.7 Kryptonated SSD. This sensor is constructed by encapsulating Kr-85 within the lattice interstices of a host material, such as platinum dioxide (PtO_2), which is overlain with a permeable plastic membrane and also attached to a p-n junction connected across a battery. As hydrogen diffuses through the membrane and the host material, Kr-85 is released. The Kr-85 changes the current in the p-n junction which is inversely proportional to the concentration of Kr-85 released. The quantity of released Kr-85 is directly proportional to the hydrogen concentration.

6.1.3 Electrochemical Detectors

This commercially available sensor is assembled using platinum (Pt) and platinum oxide (PtO) electrodes in an alkaline electrolyte. This electrochemical sensor is specific for hydrogen. Commercial versions of this detector have been used in nuclear environments.

6.1.4 Thermal Conductivity Detectors

This detector, an electrical conductor, responds to changes in the thermal conductivity (heat transfer) of the gas mixture in thermal equilibrium with the conductor. A Wheatstone bridge circuit is used to measure the resistance of the current carrying conductor at thermal equilibrium with the gas mixture. Hydrogen and helium have thermal conductivity values at least a factor of seven greater than other gases. In the absence of helium, hydrogen concentrations can be determined. Direct measurements of hydrogen can be made from a sample gas stream or dual measurements (with and without a catalyst) can be made with the difference representing the concentration of hydrogen present.

6.1.5 Absorption Detectors

Two types of absorption detectors have been identified. In the first type, hydrogen dissolves in a palladium-silver (Pd-Ag) alloy causing a volume expansion to occur. This volume expansion is used to quantify hydrogen concentrations. Hydrogen has been detected up to 20% using this technique.

In the second type, a thin film of palladium changes resistance as hydrogen is absorbed. Hydrogen concentrations to 10% have been determined and the detector has been used for corrosion assessment.

6.1.6 Ion Current Detectors

This detector uses a heated palladium (Pd) wire stabilized at 850°C. In the presence of hydrogen, an ion current flows and is detected with a microammeter. Up to 10% hydrogen in nitrogen has been detected, but a mixture of 3% hydrogen in air ignites.

6.1.7 Acoustic Detectors

Hydrogen is determined with this technique by measuring acoustic velocity at two frequencies, one at 10 MHz which is above the hydrogen relaxation frequency of 1 MHz and the other below 1 MHz. Two sets of sensors, each set a flat, right circular cylindrical transmitter-receiver (T-R) combination, are used for the measurements. Each T-R set must be isolated from each other while the T-R separation distance must be relatively small, but accurate within small tolerance levels.

6.1.8 Fluidic Detectors

The frequency of a fluidic oscillator is proportional to the square root of the molecular weight of its operating fluid and inversely proportional to the speed of sound in the fluid. A detection system specific to hydrogen is constructed by using two fluidic oscillators, one operating with the sample gas, and the other also operating with the sample gas but with the hydrogen catalytically converted to steam. Comparison of the two signals allows determination of the hydrogen concentration. Measurements of hydrogen concentrations up to 10% have been reported.

6.1.9 Summary

The upper limits of hydrogen detection in air by the various classes (techniques), are:

Thermal Conductivity	30%
Absorption	20%
Electrochemical	10%
Fluidic	10%
Solid State	10%
Ion Current	20% (H_2 in N_2)
Combustion	7%
Acoustic	---

Of the six plants visited, three used thermal conductivity, one used catalytic combustion, and two had no on-line hydrogen monitors . Electrochemical sensors have been used on a limited basis to make hydrogen concentration measurements in nuclear power plant environments.

Further development of hydrogen sensors for monitoring purposes is desirable to decrease downtime and response time, and increase accuracy, reproducibility, and specificity for hydrogen concentration determinations. In particular, hydrogen concentration measurements should be made with electrochemical, absorption, fluidic, and acoustic sensors and compared with thermal conductivity measurements.

6.2 Oxygen Monitoring Instrumentation

Two commercially available classes of proof tested oxygen monitoring instruments for on-line use in nuclear power plants are available:

- Paramagnetic
- Electrochemical

There are two sub-classes of electrochemical instruments. One sub-class uses a high-temperature oxygen diffusion electrochemical technique for detection while the other sub-class uses the more conventional polarographic/fuel cell electrochemical technique. In addition, a number of other techniques for oxygen monitoring are available for measuring oxygen concentration. These techniques include thermal conductivity and absorption. A brief summary description of some of these techniques has recently been published.[26] A brief discussion of each technique is given below. Characteristics and sources of commercially available instruments are given in Appendix B. One other technique for the determination of oxygen is available and will briefly be discussed here, although it is not appropriate for use in monitoring nuclear plants. This instrument, which is available for metallurgical investigations, converts the oxygen to carbon monoxide (CO). The infrared absorbance of CO is measured and converted to percent oxygen.

This survey has been limited to obtaining and summarizing commercially available oxygen monitoring and analysis instrumentation appropriate for on-line use in WGSs. It has not been intended as an exhaustive examination of oxygen measurement techniques, instruments, and laboratory and research devices.

6.2.1 Paramagnetic Detectors

This sensor uses oxygen's unique property of being strongly paramagnetic (factor of at least 1400) compared with other gases that have low-magnetic susceptibility. A test body filled with a gas of known susceptibility and surrounded by the sample is suspended in a non-uniform magnetic field. A null-balance, restoring current system is used to determine oxygen content. The current required to restore the test body to the null position is directly proportional to the original displacement torque; thus, the current is a linear function of the magnetic susceptibility of the sample gas. Only nitric oxide has a magnetic susceptibility that can normally interfere with an oxygen determination. Pressure variations, temperature effects, and excess vibration affect the measurement.

In a variation of the paramagnetic technique, a thermomagnetic detection system has been developed. In this system, a thermal gradient and a magnetic field gradient are created. A resistance change induced in a temperature sensitive thermistor is used to determine the oxygen concentration.

6.2.2 Electrochemical Detectors

Two sub-classes of electrochemical detectors have been identified. These are discussed separately below.

6.2.2.1 Ceramic Oxide Detectors. This sensor is fabricated by attaching porous Pt electrodes to the outside and inside of an yttria-stabilized zirconium oxide (ZrO_2) ceramic tube. At elevated temperatures, 600 to 800°C, oxygen can diffuse through the ZrO_2, setting up an electrochemical cell. In normal operation the reference gas, oxygen or air, flows on the outer side of the cathode while the sample gas flows along the outer side of the anode. Oxygen is reduced at the cathode, diffuses through the ZrO_2, and is oxidized at the anode via the half cell reactions

cathode: $O_2 + 4e \longrightarrow 2O^{-2}$

anode: $2O^{-2} \longrightarrow O_2 + 4e.$

The voltage produced is a function of the difference in oxygen's partial pressure on either side of the cell. Oxygen concentrations up to 100% can be detected, but combustibles must be absent.

6.2.2.2 Polarographic and Fuel Cell Detectors. This class of sensors represents the largest number of commercially available oxygen detectors. Both two and three electrode systems are available with the third electrode present to minimize consumption (extend the life) of the electrodes.

In the fuel cell type of electrochemical transducer, which is a galvanic device, oxygen is reduced at the sensing electrode (cathode) producing a current that is directly proportional to the partial pressure of oxygen. In the absence of oxygen, no current is produced.

In the polarographic type of electrochemical transducer, a polarizing or external voltage is applied across the measuring and reference electrodes. In the absence of oxygen, this voltage polarizes the system so the current is reduced essentially to zero. When oxygen is present in the sample gas stream, and reacts at the cathode, current begins to flow. The sensor produces a linear output signal proportional to changes in the partial pressure of oxygen. Recent developments with polarographic sensors produce an oxygen detector with relatively fast response times (90% full scale in 10 seconds), long shelf life, linear output, zero offset, and throw away disposability.

Half cell reactions for both the fuel cell and polarographic two or three electrode oxygen detectors can be summarized as follows:

Cathode: $O_2 + 2H_2O + 4e \rightarrow 4(OH)^-$

Anode: a) $M + n(OH)^- \rightarrow M(OH)_n + ne$ M = metal

b) $M + Cl^- \rightarrow MCl + e$

Reference: $4\,(OH)^- \rightarrow O_2 + 2H_2O + 4e$

Two anode reactions are written since both hydroxide $(OH)^-$ and chloride $(Cl)^-$ electrolytes are used. If a third or reference electrode is used, it is Pt. Cathode/anode electrode combinations that are used include gold/silver (Au/Ag), gold/lead (Au/Pb), carbon/cadmium (C/Cd), carbon/zinc (C/Zn), and silver/cadmium (Ag/Cd). Both types of electrochemical sensors (fuel cell and polarographic) are capable of measuring oxygen concentrations to 100%.

6.2.3 Absorption

These oxygen detection systems, which are not appropriate for continuous on-line monitoring, represent the use of wet chemical analysis for monitoring purposes. The system works by using an absorbing material that extracts oxygen from a known volume of gas sample that has been extracted from the gas stream of interest. Gas volumes measured before and after absorption by the oxygen-specific medium represent the oxygen concentration.

6.2.4 Thermal Conductivity

Thermal conductivity measurements are described in the Thermal Conductivity Dectectors Section. Thermal conductivity measurements for oxygen are of two types. In the first type, the oxygen is measured directly because its thermal conductivity exceeds that of the other component(s) (e.g., determination of oxygen in argon). In the second type, represented by hydrogen/air mixtures, two thermal conductivity measurements are made and the difference between the measurements represents the oxygen concentration. One measurement involves the determination of the thermal conductivity of the sample gas of interest while the second measurement determines the thermal conductivity of the sample gas that has been passed over a catalyst to convert the oxygen to water vapor. If necessary, hydrogen is added to ensure that all of the oxygen is converted.

6.2.5 Summary

The range of oxygen detection in air by the various classes (techniques) are

Paramagnetic	0 to 100%
Thermomagnetic	0 to 25%
Electrochemical:	
Zirconium Oxide	1 to 100%
Fuel Cell	1 ppm to 100%
Polarographic	0 to 100%
Absorption	0 to 60%
Thermal Conductivity	0 to 30%

Of the six plants visited, three employed paramagnetism, one employed an electrochemical fuel cell, and two had no on-line oxygen monitors.

Available commercial oxygen sensors are quite adequate for on-line monitoring of oxygen. With the recent developments that have occurred in fuel cell/polarographic electrochemical technology, a wide choice of sensors and systems is now available to the nuclear industry. This choice extends to both the paramagnetic and electrochemical determination of oxygen concentrations in gas streams.

7. SUMMARY OF STUDY CONCLUSIONS

Conclusions have been drawn in various parts of this study. We restate them here for convenience.

Plant Surveys (Section 3)

- No fire or explosion has ever occurred at a PWR with a Type A system whose sole treatment is gas compression and storage. There does not appear to be an ignition source internal to Type A systems.
- All plants visited have had, at one time or another, gas concentrations in the combustible range - but not routinely.
- The fire that occurred in Plant Number 4 (Type D system) would have been unlikely without the internal ignition source provided by the recombiners in the cryogenic unit. On-line monitoring of the oxygen at the recombiner also might have prevented the accident.
- The main problems observed in the WGSs studied seem primarily to arise from moisture and/or leaks. Moisture in carbon steel systems causes corrosion, eventual valve problems, and possible external leaks. In monitoring system plumbing, improperly located or sloped lines or lines too long can cause collection of moisture resulting in systems that do not work correctly.
- Sampling only just prior to a WGDT discharge is unsatisfactory in hat the onset of problem conditions, such as trends toward explosive mixtures and their initial occurrence, goes undetected. This may be particularly important in systems with known internal ignition sources (i.e., recombiners).

Risk Evaluation (Section 4)

The ranking of risks based on internal sources and explosive gas mixture inventory showed:

- WGSs having both a recombiner and high-pressure gas storage have the highest comparative risk of explosion.

- A WGS with neither a recombiner nor high pressure compressed gas storage exhibit the least risk.

Flammability and Detonation (Section 5)

- The results from a number of studies recently reported and soon to be reported promise to shed new light on the theoretical, experimental, and modeling of flammability and detonation, including limits, for hydrogen/air and hydrogen/oxygen/nitrogen mixtures. This information should be continuously evaluated for applicability to WGSs in nuclear power plants.

- Very limited experimental data exists on the effect of initial pressure on the flammability limits of hydrogen/air mixtures. The effect of initial pressure on the flammability limits of hydrogen/air mixtures needs to be validated.

Hydrogen and Oxygen Monitoring Instrumentation (Section 6)

- Instrumentation for on-line monitoring of oxygen concentrations is available and does a good job over the range parts per million (ppm) to 100%. Electrochemical and paramagnetic techniques can be used to monitor oxygen. Off-line or laboratory measurements of grab samples can be accomplished using GC.

- Thermal conductivity is presently used to monitor on-line hydrogen concentrations. Some electrochemical measurements have been made. Better and faster measurements with less downtime of the instrument and greater specificity would significantly improve the on-line monitoring of hydrogen concentrations.

General Conclusion

A general conclusion to be drawn from Sections 3, 4, and 5 is that it should be recognized that possible waste gas explosions pose a threat to PWR operations which justifies adequate control measures.

8. RECOMMENDATIONS

First, it is recommended that to the extent practical, all PWR WGSs meet the following conditions.

- Concentrations of both hydrogen and oxygen should be kept below the flammability limits (4 and 5% respectively) and automatic dilution by nitrogen gas should be provided to keep the concentrations below their limits.

- Concentrations of hydrogen and oxygen should be monitored continuously at several points in the system.

- The time spent with an out-of-service monitor should be minimized by having a redundant monitor and by provisions for expeditious repair.

- Sampling and off-line laboratory analysis of waste gas should be performed periodically (a) to verify monitor calibration, and (b) to provide measurements when the monitors are out of service.

- When the on-line monitors are out of service, the frequency of sampling and off-line analysis should be increased to allow adequate monitoring of WGS safety.

- System leakage should be minimized by periodic tests and maintenance. Maintaining a positive pressure is recommended to prevent air in-leakage.

- Risk of ignition from sources internal to this system should be minimized by electrically grounding equipment such as tanks, filters, pumps, etc., by use of non-sparking valves, and by incorporating provisions or equipment that reduces the likelihood of a recombiner being an ignition source.

- In design of WGSs, consequences of possible explosions should be minimized by shielding safety related systems from the WGS and by shielding WGS decay tanks from each other.

Second, it is recommended that regulatory requirements reflect the following considerations to ensure that safety measures are not neglected:

- Measures to control waste gas explosions should be required.
- Acceptable levels of safety can be achieved in various ways and requirements should be flexible enough to accommodate plant-specific problems and conditions.

Third, it is recommended that the minimum regulatory requirements include the following:

- The concentration of either hydrogen or oxygen should be kept below the flammability limit.
- Waste gas should be sampled or monitored at two or more locations. These locations should be at those points where high concentrations of either hydrogen or oxygen may be expected and should always include the active WGDT (e.g., the compressor outlet and the WGDT).
- Frequency of sampling and analysis should be sufficient to ensure that the flammability limits are not exceeded.
- If the concentration limit is exceeded, waste gas addition to the active decay tank should be stopped. Known potential ignition sources such as a recombiner should be shut down and the concentration reduced in a timely manner.

Fourth, it is recommended that further investigations be conducted to

- Validate the Coward & Jones results on the effects of pressure on the flammability limits, and
- Investigate improved on-line hydrogen monitoring instrumentation including electrochemical, acoustical, absorption, and fluidic

techniques. The data should be compared with data from thermal conductivity measurements.

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APPENDIX A

COMMERCIALLY AVAILABLE HYDROGEN MONITORING INSTRUMENTATION

APPENDIX A

Commercial Sources for Hydrogen Monitoring Devices

Company	Type of Device	Accuracy	Response	Drift	Sensor Ambient Temperature Limit (°C)
<u>Combustion detectors</u>					
1. AMBAC Industries, Inc. Bacharach Instrument Co. 2300 Leghorn St. Mountain View, CA 94043	Hot wire % LEL	--	--	--	--
2. Amtek, Inc. Thermax Instruments Div. 6592 Hamilton Ave. Pittsburgh, PA 15206 (415) 361-1707	Catalytic % LEL	±5% of measured values	11 sec or 90% of full scale	1% of full scale per mo.	--
3. ATO Inc. Scott Aviation Div. Lancaster, NY 14086 (716) 683-5100	Catalytic % LEL	±3%	3 sec time constr.	--	-40 to 93.3
4. Becton Dickerson & Co. Energetics Science Div. 85T Executive Blvd. Elmsford, NY 10523 (914) 592-3010	Catalytic % LEL	--	--	--	--
5. Bendix Corporation Environmental & Process Instruments Div. P. O. Box 831 Lewisburg, WV (304) 647-4358	--	--	--	--	--
6. Control Instruments Corp. 25 Law Drive Fairfield, NJ 07006 (201) 575-8114	Catalytic % LEL	±3% full scale	--	2% in 30 days	-40 to 100
7. CSE Corp. 600T Seco Rd. Monroeville, PA (412) 856-9200	Catalytic	--	--	--	--

	Company	Type of Device	Accuracy	Response	Drift	Sensor Ambient Temperature Limit (°C)
8.	Devco Engineering, Inc. 36-B Pier Lane W. Fairfield, NJ 07006 (201) 228-0321	Catalytic --	--	--	--	--
9.	Emmet Corp. 2308 S. Industrial Hwy. Ann Arbor, MI 48104 (313) 761-1270	-- Alarm	--	--	--	--
10.	Gas Tech, Inc. Johnson Instrument Div. 321 Fairchild Dr. Mountain View, CA 94043 (415) 967-6794	Catalytic % LEL	--	--	--	--
11.	General Monitors, Inc. 3019 Enterprise St. Costa Mesa, CA 92626 (714) 540-4895	Catalytic % LEL	±2% full scale	6 sec time constr.	5% per year	-18 to 66
12.	Lumidor Safety Products 5364 NW 167th St. Miami, FL 33014 (305) 625-6571	Catalytic Alarm Hot wire	--	--	--	--
13.	Mine Safety Appliances Company Instrument Division 201 N. Braddock Ave. Pittsburgh, PA 15208 (412) 273-5000	Catalytic % LEL	--	1 sec to alarm	2% full scale in 30 days	-40 to 93.3
14.	Neutronics, Inc. 452 Drew Court King of Prussia, PA (215) 275-3800	Catalytic	--	--	--	--
15.	NL Baroid Div. P.O. Box 1675 Houston, TX (713) 527-1100	Catalytic % LEL	--	--	--	--
16.	Preiser Scientific, Inc. 900 MacCorkle Ave., S.W. Charleston, WV (304) 344-4031	Catalytic % LEL	--	--	--	--

Company	Type of Device		Accuracy	Response	Drift	Sensor Ambient Temperature Limit (°C)
17. Seigler Gasalarm Div. P.O. Box 45146 Tulsa, OK (918) 663-4180	--		--	--	--	--
18. Sunshine Scientific Instruments, Inc. 1800 Grant Ave. Philadelphia, PA (215) 673-5600	Catalytic (Markets product manufactured by item 4)		--	--	--	--
19. Wemco Instrumentation Company P.O. Box 18345 Houston, TX (713) 224-2511	Catalytic	% LEL	--	--	--	--
Solid state detectors						
20. ADS Systems Inc. 12729T Salt Lake City Way Seattle, WA (206) 365-7500	Carbon granules in plastic	% LEL ppm	--	--	--	Cryogenic to 100
21. American Gas and Chemical Co., Ltd. 220 Pegasus Ave. Northvale, NJ (201) 767-7300	--		--	--	--	--
22. Calibrated Instruments Inc. 729 Saw Mill Rd. Ardsley, NY 10502 (914) 693-9232	Semi-conductor material	Alarm	--	--	--	--
23. C.I., Inc. P.O. Box 512 Detroit Lakes, MN 56501	Semi-conductor material	Alarm	--	--	--	--
24. International Sensor Technology 3201 S. Halladay St. Santa Ana, CA 94705 (714) 546-0672	Semi-conductor material	% LEL,	2% ppm	30 sec to 90% FS for ppm; 10 sec to 90% FS for % LEL	2% in 3 months	-10 to 50

Company	Type of Device		Accuracy	Response	Drift	Sensor Ambient Temperature Limit (°C)
25. Interscience Laboratory 4190 Manuela Ave. Palo Alto, CA 94306 (415) 948-7894	Semi-conductor material	% LEL,	ppm	--	--	--
26. K-F Industries, Inc. 230 W. Dauphin Philadelphia, PA (215) 425-7710	--	Alarm	--	--	--	--
27. Quantum Instruments, Inc. 1075T Stewart Ave. Garden City, NY (516) 222-0611	Semi-conduct. material	Portable leak detector alarm	--	--	--	--
	(No longer markets monitoring device)					
28. Reich Associates, Inc. 902 Avenue K P.O. Box 73 Plano, TX (214) 424-7904	--	Alarm	--	--	--	--
	(Also manufactures custom systems)					
29. Shigoto Far East, Ltd. 1500 A Broadway New York, NY (212) 840-8670	Markets detector used in devices marketed by items 23 and 25; also markets corresponding circuitry.					
Electrochemical						
30. Exo-Sensors, Inc. 23041 Alcalde Dr. Laguna Hills, CA 92653 (714) 951-1239	Nuclear industry oriented --	0-10%	±2% full scale	120 sec to 60% full scale	--	--
31. General Electric Co. Space Division P.O. Box 8555 Philadelphia, PA 19101 (215) 962-2956	Nuclear industry oriented --	0 to 10%	±0.5% full scale	2 hours to 90% response to step change at room temp.	--	--

Company	Type of Device		Accuracy	Response	Drift	Sensor Ambient Temperature Limit (°C)
Thermal conductivity analyzers						
32. Beckman Instruments, Inc. Process Instruments Div. 2500 Harbor Blvd. Fullerton, CA 92634 (714) 871-4848	Wire filament	% LEL	±2% full scale	30 sec for 90% change at 250 cc/min	±2% in 24 hour	4.4 to 38
33. Cambridge Instruments Co. Inc. 73 Spring St., Ossining, N.Y. 10562 (914) 941-8100, (212) 931-2100	Filament	0 to 25%	±2% full scale	25 sec for 70% full scale	--	0 to 50
34. Comsip, Inc. Delphi Inst. Div. 12373 E. Barringer St. S. El Monte, CA 91733 (213) 575-8092	Nuclear industry oriented Wire Filament	% LEL	±1% FS	30 sec for 90% change for percent ranges; 60 sec for 90% change for ppm ranges	±1% in 24 hour	1.7 to 48.9
35. Leeds and Northrup North Wales, PA 19454	Thermistor	0 to 1% to 0 to 100%	±2% of span	23 sec for 90% of step change	±1% of span per week	-10 to 50
36. Teledyne Analytical Instruments 16830 Chesnut St. City of Industry, CA 91748 (213) 283-7181	Filament	0 to 30%	±2.5% full scale	120 sec for 90% of reading	±2% full scale per month	4.4 to 23.9
	(System undergoing qualification to IEEE 323-1974 and IEEE 344-1975 standards)					
Absorption detector						
37. Lawrence Electronics Company 14636T Ambaum Blvd. SW Seattle, WA (206) 243-7310	Pd alloy	--	--	--	--	--

APPENDIX B

COMMERCIALLY AVAILABLE OXYGEN MONITORING INSTRUMENTATION

TYPE: Paramagnetic Oxygen Analyzers

MANUFACTURER	MODEL	RANGE	ACCURACY	RESP. TIME	DRIFT	OPERATING TEMPERATURE	NOTES
Beckman Instruments Fullerton, CA.	755	0-1% thru 0-100% over 6 ranges in various combinations.	--	adjustable to 5-25 sec normal <10 sec to 90% FS	0 drift ± 2%FS max per 24 hr. 5.0 on ±2% FS/24 hr. max	-20 to 120°F	Flow rate 50-500 cc/min.
P.K. Morgan Instruments No. Andover, Ma. Chatham,Kent,England	262D	0 - 100.0%	± 3% FS	30 sec	--	--	Medical Use.
Sybron/Taylor Rochester, New York	540A	0-1% thru 0-100% in 7 ranges	± .02% O_2 or ± 1% FS	<8 sec to 90% of step change	zero: <0.02% O_2 span: <0.5% FS per 180°F	14 - 122°F	Cell flow rate 50 - 150 cc/min. Bypass 400-7900 cc/min. medical use
	541A	0-1% thru 0-100% in 7 ranges	± .02% O_2 or ± 1% FS	<14 sec to 90% of step change	zero: <0.02% O_2 span: <0.5% FS per 18°F	14 - 122°F	Monitoring of combustion gases, allows entrainted liquids. Cell flow rate 100-150 cc/min. bypass 100-1500 cc/min.
	570A/ 580A	0-100%/0-100% in 3 ranges	± 0.1% O_2 <±1% FS	<11.5 sec to 90% of step change	zero: ±0.02% O_2/°C span: ±0.1% FS/°C	32 - 122°F	Portable
Leeds and Northrup N. Wales, PA.	7863	0-25% or less, or 20 - 30%	± 1% FS	<60 sec to 90% of step change	zero: +2%FS/wk.max. span: ±1%FS/wk.	14 - 122	Thermomagnetic

TYPE: Electrochemical Oxygen Analyzers - Zirconium Oxide (All designed for stack gas analysis - except last)

MANUFACTURER	MODEL	RANGE	ACCURACY	RESP. TIME	DRIFT	OPERATING TEMPERATURE	NOTES
Ametek/Thermox Pittsburgh, PA.	WDG-III	0.1% - 100%	± 1% of Net excess O_2	<5 sec 90% PS	<0.1%/sensor cell output month	-5 - 500°F (sensors) 0 - 120°F (control)	Sample temp up to 3200°F. Flow 47 - 5664 cc/min
	WDG-P	0.1 ppm - 100%	± 1% of meas value	<15 sec. 90% FS	<0.1%/sensor cell output month	0 - 300°F (sensor) 0 - 120°F (control)	Handheld portable sample temp to 2000°F flow .1-50 SCFH
Applied Electrochemistry Sunnyvale, CA.	S-3A	0-100.00% and 0 - 100 ppm	0.1% O_2 reading	<.1 sec 90% of value	.01% of O_2 value/24 hrs. for stable T	--	Medical
Hayes Republic	--	--	--	--	--	--	Portable and Fixed
Leeds + Northrop N. Wales, PA.	7875	0 - 99.9%	± 5% of reading or ± .05% O_2	60 sec max to 95% of (step change)	--	50-1300°F (sensor) 40-100°F (control	Flow 500 cc/min
Mocon Elk River, Minn.	LC 700F	0 - 50% in 3 ranges	± 2% FS on the 0-50 and 0-5 range or ± 3% FS on 0-.5% O_2 range.	2 sec	--	--	2-5cc sample req'd.
Teledyne Analytical City of Industry, CA.	9400	0.1 - 100%	--	2 sec max	--	--	--

TYPE: Electrochemical Oxygen Analyzers - Fuel Cell/Polarographic

MANUFACTURER	MODEL	RANGE	ACCURACY	RESP. TIME	DRIFT	OPERATING TEMPERATURE	NOTES
Anacon Burlington, MA.	76,77,79	0-10, 0-100 0-1000 ppm	± 5% FS	<100 sec to 90% FS	--	15 - 25°C	Process monitoring polarographic: Ag cathode, Cd,anode, Pt electrode, flow: 8 l/hr at .35 - 10.35 bar
Bacharach Instrument Co. Pittsburgh, PA	K25	0-25%	± 0.1% O_2	--	--	--	Portable Fuel Cell
	K525	0-5%, 0-25%	± 0.1% O_2	--	--	--	Portable Fuel Cell
	K2500	0-25, 0-100%	± 0.1% O_2	--	--	--	Portable Fuel Cell
	sensox 2	0-25%	--	--	--	--	Industrial safety - handheld polarographic
Beckman Fullerton, CA.	OM Series	0-100% and other options	± .5% - 2% FS depending on range	.1-20 sec. to 90% of step change	--	--	Medical
	700 & 7000 Series	0-1% to 0-25% in 4 ranges	± 1% FS at T or ±6%FS over full T range	<20 sec to 90% of step change	--	32-110°F (sample) 32 - 122°F (Control)	Process monitoring Polarographic: Ag Anode, Au cathode, KC Electrolyte
Bendix Environmental & Process Institute Lewisburg, W.VA.	305	0-100%	± 1%	30 sec	± 1% / 24 hrs or ± 5%/ΔT	0 - 50°C	Polarographic Disposable Cell
Biomarine/Rexnord	200 Series	0-25% or 0-40%	± 1% O_2	<10 sec to 90% of step change	--	32 - 104°F	Portable - Industrial Safety
	900 Series	0-25% or 0-40%	± 1% O_2	10 or 20 sec	--	5 - 104°F	Portable also detects combustable gases.
Chemical Sensor Development Torrence, CA.	Coulox-meter	0-1 to 0-1000 ppm (with attenuator .1 to 100%)	--	<60 sec to 90% of step change	--	--	Lasts 10,000 hrs at 10 ppm O_2, rechargeable

TYPE: Electrochemical Oxygen Analyzers - Fuel Cell/Polarographic

MANUFACTURER	MODEL	RANGE	ACCURACY	RESP. TIME	DRIFT	OPERATING TEMPERATURE	NOTES
Delta F Woburn, MA.	PA-10025A	0 - 25%	± 2% FS analogue display ±1% FS digital display	<60 sec	Negligible	32 - 150°F	5 Yr. warranty. Temp controller available KOH Electrolyte
Dynamation Ann Arbor, MI.	Combo 033	--	--	<30 sec to 90% of value	--	0 - 100°F	Portable - checks for O_2 deficiency alarm only polarographic
	LCD combo	0 - 100%	--	<30 sec to 90% of value	--	15° - 120°F	Portable - checks O_2 & LEL built in Alarms, polarographic
Energetic Science, Div. of Becton Dickinson Elmford, N.Y.	Ecolyzer 400	0 - 25%	± 0.2% O_2	<15 sec to 90% of value			
	Ecolyzer 600	0-25% or 0-50%	± 0.2% O_2	<15 sec to 90% of value			
Enmet Ann Arbor, MI	WOA-10	0-2.5% and 0-25%	--	--	--	--	Designed for O_2 deficiency (portable)
	CGS-10	--	--	<22 sec to 90% of value	--	14 - 122°F	Designed for O_2 deficiency (portable) also toxic gas
Gas Tech Mountain View, CA.	GX-3	0-25%	--	--	--	--	Diffusion Type
	1214	0-25%	--	--	--	--	Diffusion Type
	1313	0-25%	--	--	--	--	Diffusion Type, but O_2 only
	1641	0-30%	± .5% O_2	4 sec 21% to 0%	--	--	Diffusion Type, req's sample flow 1 l/min.

TYPE: Electrochemical Oxygen Analyzers - Fuel Cell/Polarographic

MANUFACTURER	MODEL	RANGE	ACCURACY	RESP. TIME	DRIFT	OPERATING TEMPERATURE	NOTES
GC Industries Chatsworth, CA.	33-500	0-25%	±0.5%	6 sec	--	0 - 50°C	Fuel Cell, 6 mo. Lifetime
MSA Pittsburgh, PA.	260	0-25%	--	<20 sec to 90% of value	+5% FS 0-40°C	--	Designed for toxic warning + O_2 (portable)
	E	0-25%	± 2% FS or 0.5% O_2	--	--	--	Zinc cathode, carbon anode for O_2 deficiency or leakage
	S	5-40%	± 5% FS	--	--	--	" " "
	245	0-25%	± 1% FS at T ± 5% FS over 0-400°C	-- <20 sec to 90% of value	-- --	-- 0 - 125°	
Neotronics N. S., Inc. Jefferson, GA.	950-1	--	--	60 sec.	--	--	Portable Electrochemical - alarm for deficiency
Neutronics, Inc. King of Prussia, PA.	950	0 - 35%	± 0.5% FS	<15 sec 90% FS	zero: <0.5% FS/day but <2%/month span: <1% FS/day but <3% FS/month	5°C - 55°C	Explosion proof fixtures available Fuel Cell 9 - 12 mo. life, user setable alarm/relay.
Sum X Corp Austin, Texas	500	0.1% - 99.9%	± .02% O_2	--	--	--	Portable, measurement in gas or liquid, also measures temp from 0.01° - 50.0°C Cathode reduction in membrane-covered cell

TYPE: Electrochemical Oxygen Analyzers - Fuel Cell/Polarographic

MANUFACTURER	MODEL	RANGE	ACCURACY	RESP. TIME	DRIFT	OPERATING TEMPERATURE	NOTES
Teledyne Analytical City of Industry, CA.	326 series	Any 3 ranges from 0-100%	± 2% FS ± 5% of reading over T range	<7 sec to 90% of scale	<± 2% of value per month	±32°-122°F	Available in Bulkhead + NEMA enclosures
	320	APPROXIMATELY	THE	SAME SPECS	AS 326		Portable
	328	"	"	" "	" "		Explosion Proof
	333	"	"	" "	" "		Pocketsize - alarm only for deficiency
	335	"	"	" "	" "		Designed for closed environments - on line monitoring

TYPE: Absorption Oxygen Analyzers

MANUFACTURER	MODEL	RANGE	ACCURACY	RESP. TIME	DRIFT	OPERATING TEMPERATURE	NOTES
Bacharach Pittsburgh, PA	Fyrite	0 - 7% 0 - 21%, or 0 - 60%	± .5% O_2 ± .5% O_2 ± .5% O_2	3 sec	--	-30 - 150°F	Hand sampling only Portable
Burrel Pittsburgh, PA	40-580	1/2 - 20%	± 1/4% O_2	--	--	--	Hand sampling only Portable
Hays Republic Michigan City, IN.	A-00621A	0 - 20%	± .1% O_2	--	--	--	Combustion Gas Analysis

TYPE: Thermal Conductivity Oxygen Analyzer

MANUFACTURER	MODEL	RANGE	ACCURACY	RESP. TIME	DRIFT	OPERATING TEMPERATURE	NOTES
Comsip Whittier, CA.	K-IV	0-10%, 0-25% or 0-30%	± 5% FS	<60 sec to 90% FS	zero and span: ± 2%/week	40°-120°F	Designed for containment buildings -10^6 rads total exp rating, remote sensor temp 150°F post LOCA
Teledyne Analytical City of Industry, CA.	225 (O_2/A)	--	--	--	--	--	Special configuration available for containment buildings

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A study has been performed to evaluate problems assiciated with the existence of flammable or explosive gas mixtures in Pressurized Water Reactor waste gas systems. Information on existing waste gas systems, waste gas concentrations, and gas monitoring instrumentation obtained from six operating nuclear power plants is summarized. A comparative risk evaluation has been performed for several generic types and configurations of PWR waste gas systems. Waste gas systems in the plants visited are included and categorized as part of the risk evaluation.

Existing data on the effect of initial pressure on flammability limits, as well as recently reported data on flammability and detonability of hydrogen/air mixtures has been collected and summarized. A survey of commercially available instruments for monitoring hydrogen and oxygen concentrations has been performed and the results tabulated. A series of observations, conclusions and recommendations are given.

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