IMPACTS OF COOLING WATER QUALITY ON OPERATIONAL SAFETY OF WATER COOLED REACTOR

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ABSTRACT

Cooling water chemistry and its effects on fuel elements cladding and reactor components materials performance are important factors for safe and reliable operation of nuclear reactors. This is because; at elevated temperature, water is an aggressive medium and may causes corrosion problems in fuel elements cladding and reactor structural materials. For this reason, reliability and safety for nuclear power and research reactors are achieved by using proper fuel cladding and structural materials. Also, cooling water regimes must be adjusted and proved to prevent dangerous corrosion problems. In this paper, a comparative technical evaluation study among different reactor types concerning cooling water specifications in case of regulatory standard values and operating experience conditions have been investigated. Cooling water specifications for various types of nuclear reactors and impacts of abnormal cooling water quality on reactor materials have been reviewed and discussed. Measures adopted to prevent or decrease water impieties accumulation have been implemented. For further cooling water quality improvements to reduce radiation dose from primary circuits and to achieve higher burnup and better fuel performance, constitution of LWR chemistry guidelines and a new pH control method for primary coolant have been recommended.

INTRODUCTION

Water is used as a primary coolant in most of nuclear power and research reactors and as a medium in the secondary circuit as well as in associated auxiliary systems. At elevated temperatures water is an aggressive substance when it is in contact with structural materials, which means that the reliability of many systems in nuclear power plants depends strongly on cooling water control. It is especially important for primary circuits and fuel cladding. Water coolant chemistry and corrosion problems are issues of special importance in the safe and reliable operation of nuclear power plants. So that water regimes for commercial water cooled reactors must be developed and proved to be satisfactory. Normally, reliability and safety are achieved by using proper fuel cladding and structural materials and by taking special measures to prevent dangerous corrosion, erosion and other processes. In recent years a growing interest in this problem has again been observed. For this purpose reliable and safe cooling water regimes have been developed for water cooled reactors. However, the operational experience of nuclear power water cooled reactor showed that after a certain period of time even under normal working conditions some undesirable influences can take place. Among these effects and of special interest are fuel element cladding integrity deterioration and steam generator tube failure due to corrosion, erosion, hydrating and deposition on heat transfer surfaces of corrosion products and other coolant impurities.

Recently, nuclear water power reactors experience showed that after a certain period of time even under normal working conditions some undesirable influence in fuel element cladding integrity can take place due to corrosion, erosion, hydriding and deposition on heat transfer surfaces of corrosion products and other coolant impurities. Studies are continued and new R&D work is being conducted based on operational experience for further improvement of the technology and a better understanding of the physico-chemical nature of those processes. Also various technical options of water chemistry is farther diversified and complicated by the increase in nuclear power plants of different types. For this purpose it is required to clarify the knowledge, experience and technical basis about cooling water chemical specification for the safe and reliable operation of nuclear reactors and for realizing the water chemistry operation guidelines for water cooled reactors (1-3).

WATER QUALITY CONTROL FOR WATER COOLED REACTORS

1. Impurities in Reactor Coolant Circuits

High purity water coolant should ensure adequate corrosion resistance of all the materials used (stainless and carbon steels, zirconium, copper, nickel alloys, etc.). However migration and transport of irradiated corrosion products and other impurities in the reactor core lead to the formation of highly radioactive deposits in some parts of the primary circuit and to radioactive contamination of primary pipes and equipment (especially in BWRs). This causes difficulties in maintenance and repair because of the high radioactive dose and necessitates decontamination of some equipments and even the primary circuit as a whole. More serious problems connected with the interaction between water coolant and cladding material might occur under abnormal conditions, for instance, the zirconium alloy/water coolant reaction during the Three Mile Island accident led to cladding failure and hydrogen formation.

The wish to decrease radiation doses from primary circuit equipment and piping has led to new efforts to improve water chemistry. Development of advanced water reactor concepts to achieve higher burnup and better fuel utilization also requires additional safety measures because of the longer residence time of fuel in the reactor, in some cases the higher temperature of the coolant, the possibility of nucleate boiling in PWRs, etc. Normal operational conditions related to water chemistry may be achieved by:

(1) Use of corrosion-resistant materials for fuel cladding and other components and piping in contact with water coolant in the primary and auxiliary systems,

(2) Cooling water chemistry control by means of various additives to reduce the corrosion processes and the influence on behavior of impurities in the circuits, and

(3) Effective coolant purification systems to remove undesirable impurities.

Table 1 shows the sources of impurities that could enter into the reactor and the measures that could be taken to prevent or decrease the accumulation of impurities (1).

Table 1: Impurities in reactor coolant circuits

Source of impurities	Chemical composition of impurities	Measure s to prevent or decrease impurity accumulation
Initial water for circuit	Soluble salts and gases (Na', K* Mg^{2}*, Ca^{2}', Cl-, NOi, SiOi, **Oi,** N,, CO^.etc	Efficient purification of water
Make-up water	Soluble salts and gases (Na'.K^.Mg^Ca^.Cr, NOi, Si03, 0,, Ni, COa, etc.)	Efficient purification of water
Cladding materials	Corrosion products Uranium and fission products due to surface contamination during fuel fabrication	Suppression of corrosion by water conditioning Surface cleaning during fuel fabrication
Structural materials (heat exchanger, pipes, vessels, etc.)	Corrosion products: Fe,Co,Cr,Ni,Mu, Cu, etc.	Suppression of corrosion by water conditioning
Pressurizers (for PWRs)	O_2 , N_2	Use of pure helium or vapor pressurizers
Coolant and condensate purification systems	Fine filter materials	Use of traps
Cooling water and air ejection in vacuum part of turbine	Salts, particulate matter, air	Improvements in sealing of turbine and condenser
Chemical additives for conservation, decontamination, etc.	Acids, alkalis, salts	

2. Water Chemistry Control in Water Cooled Reactors

2.1 LWRs

Water chemistry in PWRs should guarantee the integrity and reliability of the primary circuit and fuel element cladding. However, certain factors relating to more precise control should not be overlooked, one of which is the co-ordination of lithium and boron concentrations in the primary circuit to maintain the pH within a narrow range during reactor operation. It is advisable to amend coolant chemistry specifications to allow a constant and high pH value to be maintained throughout reactor operation, correlating the alkali level with the boron concentration. Such practice exists for all USSR PWRs and good experience is known to have been achieved in Japan (4).

Boron is added to the system as a long term (shim) poisons. During first year operation concentrations up to 4 mg B/kg counteract the excess of the initial fuel load. In some PWRs where sub-cooled boiling occurs, enhanced corrosion of Zircaloy cladding can be observed. Hydrogen can be stripped off from the water phase to the steam bubbles, resulting in local reduction of the hydrogen concentration with a corresponding increase in the concentration of oxidative radicals (NOx). Therefore, it was recommended that attention be paid to limiting the NOx-ions concentration, since this is an indicator of the specific oxidation processes in the reactor coolant. As an example, the recommended pH control method of PWR primary coolant is shown in Fig. 1. The pH control method was determined from the three points of view, i.e., the integrity of nuclear reactor structural material, the soundness of fuel cladding, and the dose-rate reduction. On the other hand, the limited value of secondary system was defined from a viewpoint of the integrity of a steam generator and secondary system instrument.

Experience from primary coolant and feed water impurity concentrations in the different LWRs showed that the neutral water chemistry regimes guarantee reliable and safe operation of the fuel elements and other reactor components (1,2,5,6). However, crud depositions on the fuel elements were observed in some cases when specifications of water quality were disregarded. Experience also showed that the presence of copper impurities produces some trouble in BWR operation. For this reason it is necessary to limit and even to eliminate the use of copper-containing alloys in the feed system. Of great importance for BWRs is an effective feedwater purification system and measures for reducing crud levels during transient periods and shutdowns. The attempt to limit corrosion in the feedwater system by adding certain amounts of oxidizing agents to the turbine condensate has proved useful. Use of magnetic filtration for removing insoluble corrosion products remains of potential interest. This is important for the purification of high temperature condensate drains before being mixed with the feedwater. As seen from Table 2, experience in LWRs showed that the neutral water chemistry regime guarantees reliable operation of the fuel elements and other components (2).

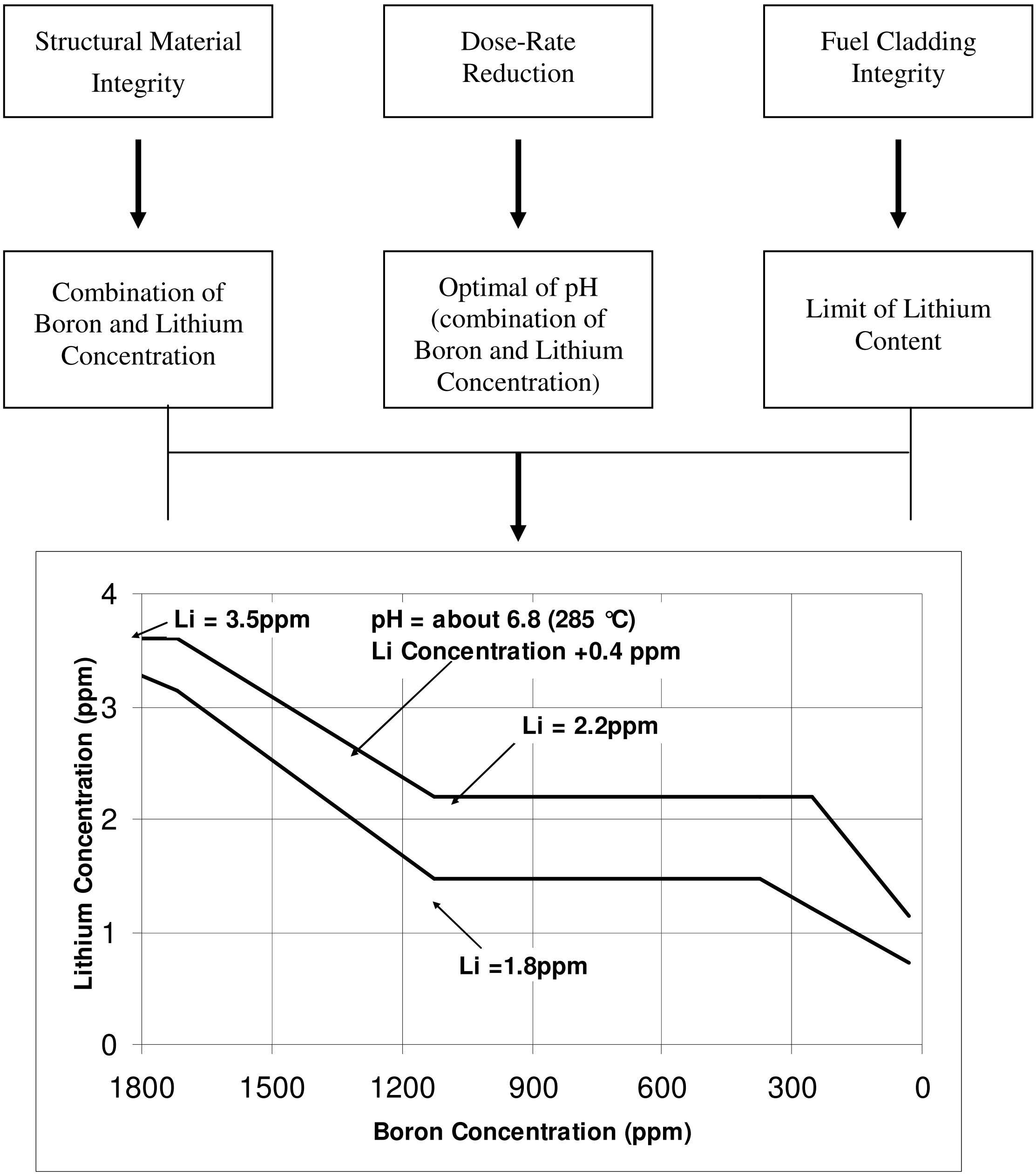
Structural Material Integrity
Dose-Rate Reduction
Fuel Cladding Integrity
Combination of Boron and Lithium Concentration
Optimal of pH (combination of Boron and Lithium Concentration)
Limit of Lithium Content
Li = 3.5ppm
pH = about 6.8 (285 °C)
Li Concentration +0.4 ppm
Li = 2.2ppm
Li =1.8ppm
Lithium Concentration (ppm)
0
1
2
3
4
1800
1500
1200
900
600
300
0
Boron Concentration (ppm)

Table 2: Cooling water specifications for different power and research reactors [modified after Ref. (2)].

Cooling Water Specifications	**PWR**	**BWR**	**WWER-440**	**CANDU**	**Research Reactor**
Conductivity at 25°C	4 - 80 µS/cm	<1.0	**9.5 - 10.5 at 25 °C** **7..1 – 7..3 at 25 °C**	–	**1-3 µS/cm** **[< 2 µS/cm]**
pH at 25°C	5.4 - 10.5 **[4..2 - 10..5]**	5.6 - 8.6 **[5.6 – 8.6]**	NS **[9.5 – 10.5]**	**[6-9 – 10.5]**	**5.5 – 6.5 [5.5 – 8]**
Dissolved oxygen[3]	<0.1ppm **[< 5 ppm]**	100 - 300 ppb **[20 – 200 ppb]**	<10 ppb **[< 10 ppb]**	15-20 µg / kg **[< 10 ppb]**	–
Chloride	<0.15 ppm	≤100 ppb	<0.1 ppm	–	**< 1 ppm [< 0.5ppm]**
Fluoride	<0.15 ppm	–	<0.1 ppm	v	-
Dissolved hydrogen: (a) Coolant above 100°C (b) 24 h before shutdown when it is intended to open the vessel (c) Coolant below 100°C when the vessel is to be opened	25 to 50 cm^3 (NTP) per kg H_2O >15 cm^3 (NTP) per kg H_2O <5cm^3(NTP) per kg H_2O **[25 – 35 cm^3/kg]**	– – –	30 to 50 cm^3 (NTP) per kg H_2O **[30 – 60 mL/L]**	– **[3 – 20 mL/L]** –	– – –
Crud	<1 ppm **[5ppb]**	7 – 30 ppb **[40 – 500 ppb]**	NS **[50 ppb]**	– **[100 ppb]**	–
Li^{7}OH	0.7 to 2.2 ppm Li (lO^{-4} to 3.2X lO^{-}M)	–	-	1 mmg/kg DTO	–
Boron	0 to 2500 ppm **[0 – 4000ppm]**	–	0 to 12 g per kg **[0 – 12000 ppm]**	–	–
Silica	<0.2 ppm	< 2000 ppb	–	–	–
Al	<0.1 ppm	–	–	–	- **[< 0.05 ppb]**
Ca	<0.1 ppm	–	–	–	–
Mg	<0.1 ppm	NS **[1 – 50ppb]**	–	–	–
Cu	–	**NS**	–	–	<0..02 ppm **[<0.05 ppm]**

– = Not Specified

Values in parenthesis are indicating to elemental concentrations of impurities for actual operating conditions in water cooled reactors.

2.2 CANDU reactors

Several good corrosion resistant materials are used in CANDU reactors primary circuit. Although corrosion resistance is an important criterion in the selection of every material, it is not the only one. Thus, for example, neutron economy dictates the use of zirconium alloys for pressure tubes and fuel cladding and high tensile strength determines the use of 400 series steel for pressure tube end fittings. The use of carbon steel for piping and vessel shells is an inherent feature of the CANDU system. Nickel alloy tubing is used in the steam generators and other heat exchangers. For such a mixture of materials, the optimization of proper primary coolant chemistry could be possible by having a separate moderator system to which the addition of soluble poisons for reactivity control is confined. The two major requirements for chemistry control are:

i) Minimizing dissolved oxygen to ensure acceptably low rates of zirconium alloy corrosion and the avoidance of both carbon steel pitting and stress corrosion cracking of austenltic alloys; and

ii) Maintaining alkaline conditions which reduce general carbon steel corrosion rates to acceptably low levels and minimize the transport and activation of corrosion products. The suppression of radlolytic oxygen in water reactor coolants by addition of hydrogen is a well understood phenomenon. Hydrogen gas is added to the CANDU primary coolant and isotopic exchange produces dissolved deuterium. The objective is to maintain a deuterium concentration of 3 to 10 mL/kg to reduce the dissolved oxygen to acceptably low levels. The heavy water downgrading of 1 to 2 wt % has an acceptably small effect on fuel burnup. Valuable information on the required minimum dissolved deuterium concentrations has come from the periods of pressurized operation of the 25 MW(e) CANDU Nuclear Power Demonstration plant, NPD, where there is normally no hydrogen addition. The recorded deuterium concentrations are normally below 0.5 mL/kg with dissolved oxygen concentrations of 15 - 20 μg/kg (0.01 - 0.015 mL/kg) (3,7).

Lithia is added to the coolant to give a concentration of about 1 mg Li/kg D_2O which corresponds to a light water room temperature pH of 10.15. In heavy water the pertinent unit is pD but in fact what is measured is an "apparent pH" since a meter calibrated with light water solutions is used to monitor heavy water solutions. The "apparent pH" is the light water pH plus 0.3 and the true pD is the "apparent pH" plus 0.4. For convenience the term pH will be used in this paper to mean "apparent pH". So in a heavy water solution 1 mg Li/kg D_2O of lithium gives a pH of 10.45. The recommended alkalinity range is 10.3 to 10.8. The high coolant pH reduces activation, general corrosion of components and hence reduces corrosion product transport. However, if concentration of the alkali occurs, corrosion can be aggravated. The local attack on some pickering pressure tubes at contact areas with fuel bearing pads has been attributed to local crevice boiling, causing high concentrations of lithium hydroxide(8).

2.3 Secondary side water chemistry and material performance

Steam generator tube failures in water cooled power reactors result in the transfer of radioactive materials from the primary coolant system to the steam generator secondary side water, and necessitate downtime to locate and plug failed tubes. For a CANDU plant, any steam generator tube failure results in an additional economic penalty through the loss of heavy water.

The inverted U-tube steam generator has shown itself to be susceptible to tube failures. The latest annual AECL review (4) of steam generator tube failures shows that, to the end of 1980, over 60% of all operating nuclear power plants had shown some form of steam generator tube failure and 1.65% of all steam generator tubes had failed. Nearly all of the failures were attributed to secondary side water chemistry conditions and excursions, many of which resulted from condenser cooling water ingress. The choice of materials in the condensers, feedwater heaters and reheaters may also have contributed.

Table 3 demonstrate a comparison among different water cooled reactor types concerning number of steam generator ruptured tubes as an indicator for steam generator performance and cooling water quality. To date, the CANDU steam generator tube performance has been outstanding when compared to worldwide light water reactor operating experience as Table 3 shows. Of the CANDU failures, 47 have occurred in recent years at NPD. Only eight of the remaining 16 tubes have actually leaked, two at Douglas Point, one at Pickering 'A' and five at Bruce 'A'. These plants all have good quality condenser cooling water, from Lakes Huron and Ontario or the Ottawa River, and all have had exceptionally good condenser and condenser tube performance (4,9).

Table 3: Steam generator tube performance for water cooled reactors (4,9)

Reactor type	No. of reactors	No. of Steam/ Generator tubes	No. of tubes defects	% of tubes with defects
PWR & BWR	85	1 061 688	22 344	2.1
CANDU	12	300 599	63	0.02

RESULTS AND DISCUSSION

BWR water chemistry guidelines consist of three volumes, i.e., (1) BWR water chemistry guideline, (2) BWR water chemistry at startup and shutdown, a cold-and-warmth shutdown, and hydrogen injection, (3) Zinc injection and Noble-metals injection aiming at the reduction of radiation exposure and SCC inhibition, as shown in Table 4. On the other hand, PWR water chemistry guidelines consist of rout volumes. From a viewpoint of the integrity of nuclear reactor structural material and fuel cladding, (4) PWR primary water chemistry guideline, (5) PWR primary water chemistry guideline at startup and shutdown were drawn up. From the viewpoint of steam generator integrity and dose-rate reduction, (6) PWR secondary water chemistry guideline" and (7) PWR secondary water chemistry guideline at startup and shutdown were drawn up.

Table 4: Constitution of Light Water Chemistry Guidelines

Type of Reactor		**Operation Condition**	**Measures to Prevent or Decrease Impurities**
BWR		Normal Operation	Efficient purification of coolant
		Startup and Shutdown, Cold-and Warmth-Shutdown, Hydrogen Injection	Efficient purification of coolant
		Zinc Injection, Nobel Metal Injection	Suppression of corrosion by water conditioning
PWR	**Primary System**	Normal Operation	Efficient purification of coolant - Chemical additives
		Startup and Shutdown	Suppression of corrosion by water conditioning
	Secondary System	Normal Operation	Use of pure Helium or vapor pressurizer - use of traps
		Startup and Shutdown	Chemical additives

As an example, the limited value of water qualities during the normal operation time is shown in Table 5. A setup of limited values of water qualities was defined from the three points of view, i.e., the integrity of structural material integrity, and the soundness of fuel cladding, and the exposure reduction, and the technical bases were specified. The permissible maximum value of water qualities was defined in order that "a level 1" might maintain the integrity of a plant, and "a level 2" are the limited values for maintaining the integrity of a plant. The recommendation value 1" is a desired limited value defined in order to usually maintain an operating standard. On the other hand, "the recommendation value 2" is a policy objective value on the water chemistry control which can be attained over a long period of time in good operational condition. Concerning the new technology of Zinc injection and Noble-metals injection, it focused on arranging the present knowledge.

Table 5: Recommended values for water chemistry specification of LWR coolant

Control Item	Level 1	Level 2	Recommended Value 1	Recommended Value 2	Measurement Frequency
Conductivity (µS/cm)	≤ 10	≤ 1	≤ 0.4	≤ 0.15	Continuation
pH (25°C)	4-10	5.6-8.6	—	—	D
Cl^- (ppb)	≤ 500	≤ 100	—	≤ 15	W
SO_4^{2-} (ppb)	—	—	≤ 100	≤ 10	M
Silica (ppb)	—	—	≤ 1,000	—	W
Dissolved Oxygen (ppb)	—	—	≤ 400	—	D
Impurities of Metal (ppb)	—	—	≤ 200	—	W
I131 (Bq/g)	—	—	—	—	W
Boron (ppb)	—	—	≤ 200	—	M

Notes:
D = 1 time/ day-measurement.
W = 1 time/ week-measurement.
M = 1 time/ month-measurement.

CONCLUSIONS AND RECOMMENDATIONS

The coolant chemistry must be monitored and controlled in order to reduce the amount of deposited crud and the oxygen potential. The assembly design must optimize thermohydraulic parameters which reduce local coolant temperatures. Modified zirconium alloys should have a higher creep resistance without degrading the corrosion behavior. Interaction between fuel element cladding and water coolant plays an important role in normal operation, can have a dominant role in accident situations and can lead to failure of fuel rods and activity release. Existing experience showed that there were no significant problems related to the water coolant chemistry in power reactors.

In the future, the tendency will be to increase the coolant temperature, to extend the fuel residence time in the reactor core (for burnup extension) and to increase the heat flux. This can lead to an increased probability of fuel failure due to waterside corrosion, corrosion product accumulation and deposition. To prevent cladding failures under new conditions, either more resistant cladding alloys should be used or improvements in water chemistry should be introduced. Additional analysis and research are required to understand the process of corrosion products behavior and the development of an overall model of the physico-chemical processes in reactor circuits.

Seven guidelines drawn up so far are recommended and combined together into three volumes: LWR primary system, and PWR secondary system. Moreover, water chemistry standardization will be attained about "water quality analysis", "water chemical management", and "corrosion potential distribution in LPR and in-core".

For safety considerations, the following should be recommended:

1- Continuous primary cooling water purification processes according to the records of monitoring water radiochemistry specifications.
2- Implementation of an effective radiological protection programme for reactor workers and operators.
3- Achievement of a time -scheduled operational safety programme for this reactor to avoid over increase of cooling water radiological specifications.
4- Development of an efficient high level waste strategy for the reactor liquid wastes.
5- Application of a comprehensive and effective inspection, testing and maintenance programmes for this type of research reactors.
6- A well-trained staff of reactor operators and workers capable for responding in a timely and effective manner timely to any abnormal conditions.

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