The Indian Nuclear Power Programme is mainly based on the Pressurised Heavy Water Reactor (PHWR) technology. The major chemical problems that are encountered in a PHWR are: 1. Radiolysis in the Moderator System 2. Growth of the radiation fields on the out-of-core surfaces of the coolant system due to the fission products and the activated corrosion products and 3. Perturbations in the Water Chemistry Parameters of the Steam Generators (SGs) as a result of the ingress of the condenser cooling water into the feed and condensate system. The published literature in the above mentioned problematic areas of a PHWR is very scanty and no systematic data have been reported for any operating PHWR. Hence, an in-depth study of the above problems has been undertaken with a view to understanding the basic mechanisms of various phenomena related to water chemistry and also to suggest further improvements. The work reported in this thesis is mainly concerned with the chemical problems encountered in the reactor at Madras Atomic Power Station (MAPS), a typical PHWR.

The decomposition of either heavy water or light water due to radiation depends on the chemical purity and also on the type of ionic impurities. Data have been generated on how the increase in the conductivity (measure of ionic impurities present) of moderator heavy water promotes radiolysis and increases the $D_2$ and $O_2$ concentration in the cover gas during reactor operation. The relationship
between nitrogen content (indicator for air ingress) and deuterium concentration in the cover gas is also studied and data presented. To minimise corrosion in carbon steel and Monel-400 of the coolant system, dissolved oxygen in the system heavy water is to be controlled. From the data obtained on the dissolved oxygen content in the coolant water, it is inferred that better control could be achieved with nitrogen as cover gas in the place of helium. The possible mechanism for this phenomenon has been discussed.

The release of the fission products into the coolant system from the fuel has been studied in detail under various operating condition of the reactor and the data are reported here. The various techniques/methods for the detection of failed fuel have been reviewed and discussed. A method for the characterisation of the releases of radioisotopes of iodine from the PHWR fuel has been suggested.

MAPS is the first PHWR in India to use sea water for condenser cooling. Hence, the corrosion problems in the SGs due to the sea water ingress from the leaky condenser tubes are expected to be very severe in the absence of proper chemical treatment. The reactor at MAPS is also the first PHWR to install the Condensate Polishing Plant (CPP) in the feed water and condensate system to remove the ionic impurities caused by the ingress of seawater. The performance of the CPP under neutral conditions viz., in the Boiling Water Reactors has been well established and also
its performance in the secondary side of the Pressurised Water Reactors with ammonia as an alkalisng agent has been studied. However, neither any operating data nor experience is available with morpholine which is used as the agent for pH maintenance in Indian PHWRs. Differences exist in the chemical and physical properties between ammonia and morpholine. Hence, a systematic study has been undertaken with a view to framing the guidelines and optimising the performance of CPP with morpholine as the alkalisng agent in the feed water and condensate system.

It is hoped that the present work reported in this thesis contributes significantly towards better understanding as well as for the minimisation of the problems attributable to the Water Chemistry in the Indian PHWRs.