

Hydrogen generation by gamma irradiation of aqueous turbid solution of titanium

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Irradiation of titanium metal turbidity (aqueous suspension) by Co γ radiation generated a significant quantity of hydrogen. Titanium turbidity containing particles of micron/submicron size was generated by stirring titanium metal powder at 70°C in water and was exposed to γ radiation dose. Yield of radiolytic hydrogen, $G(H_2)$ was estimated by gas chromatography. In the presence of Ti turbidity, 10–20 times increase in hydrogen generation was observed as compared to that in plain or pristine water. $G(H_2)$ was found to increase with concentration of Ti turbidity. Gas to liquid volume ratio (G/L) of 1.0 was found to be optimum for maximum hydrogen yield. Effect of γ radiation dose on total H_2 yield and $G(H_2)$ was studied. Interference with hydrogen and hydroxyl radical recombination due to the reactivity of Ti^{3+} with hydroxyl radical seems to be the primary reason for enhanced radiolytic hydrogen production. Methanol addition to Ti turbid solution appears to increase hydrogen generation by almost 100 times. An outlay for medium scale hydrogen generation using γ radiation energy is also being worked out.

Keywords: H_2 generation, methanol, radiolysis, γ radiation dose, water.

As a solution to depleting fossil fuel reserves, increasing pollution and global warming, hydrogen (H_2) is regarded as the clean fuel of the 21st century. Water splitting using gamma ray energy is one of the methods of hydrogen generation. In water-cooled nuclear power plants, a small portion of water (D_2O or H_2O) is converted into hydrogen due to radiolysis. This hydrogen is vented out in boiling water reactors. Due to safety reasons, in pressurized heavy water reactors, it is recombined to form water, as more than 4% concentration of H_2 in air can be inflammable¹. Radiolytic hydrogen yield, $G(H_2)$ (molecules of hydrogen formed per 100 eV of energy absorbed) of pure water in a closed system is very low (~ 0.02) due to reaction of H_2 with $\cdot OH$ radicals². It can be increased to 10–30 times by (i) adding an $\cdot OH$ radical scavenger, (ii) by

adding nano size dispersants/turbidity such as metal oxides which can generate an electron (e^-)/hole (h^+) pair on γ irradiation and release electrons by trapping holes inside it, which further enhance H_2 production^{3,4}, (iii) by adding a catalyst which helps in combination of H atoms resulting from water splitting⁵, (iv) by lowering energy of γ rays suitable for H–OH bond cleavage with the help of array of heavy metals from MeV to eV (ref. 6). Suspension of certain metal oxides (metal turbidity) in water to some extent fulfils the above requirements. Hence, γ ray energy from nuclear reactors or high level radioactive waste, which in normal course is hazardous to health, can be utilized for medium-scale hydrogen production by radiolysis of water containing metal oxide suspension/turbidity. As titanium oxide was used for photolytic hydrogen generation⁷, aqueous Ti suspension was tested for optimizing the H_2 yield⁴.

Under certain operating conditions in nuclear power plants, due to erosion and corrosion of structural materials, metal turbidities are generated in moderator/coolant water systems. An increase in metal turbidity beyond a certain level can lead to increased hydrogen yield due to increased radiolysis of water⁴. This is due to the increase in ionic or particulate impurity in water leading to higher radiolytic dissociation⁸. In our earlier studies on the impact of different metal turbidities on radiolytic hydrogen generation in nuclear power plants, titanium turbidity was found to give maximum hydrogen yield compared to other metal turbidities, viz. Fe, Cu, Ni, Al and Cr (Figure 1). Hence, Ti was selected for the present study⁹. The results of this study are presented and a schematic of the pilot plant useful for radiolytic hydrogen production is given here.

For preparing titanium turbidity, activated titanium metal powder (after initial washing with dilute hydrochloric acid) was stirred vigorously in nano pure water on a hot plate at 70°C for 20–30 h and subsequently the sample

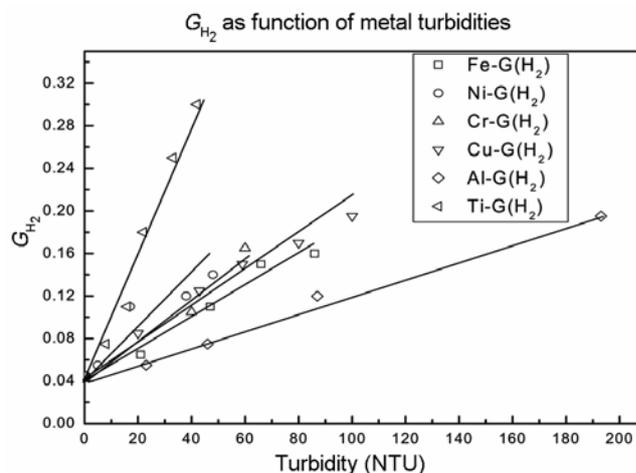


Figure 1. $G(H_2)$ as functions of metal turbidities.

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Table 1. Hydrogen generation by radiolysis of Ti turbidity

Dose (kGy)	20 NTU Ti turbidity						40 NTU Ti turbidity			
	<i>G/L</i> = 2.0		<i>G/L</i> = 1.0		<i>G/L</i> = 0.5		<i>G/L</i> = 2.0		<i>G/L</i> = 1.0	
	H ₂ (μL)	G(H ₂)								
3.7	12.2	0.26	16.7	0.28	13.6	0.15	14.3	0.30	21.0	0.32
7.4	19.5	0.21	28.0	0.21	24.6	0.13	20.2	0.20	33.1	0.25
11.1	22.4	0.16	31.0	0.16	27.2	0.10	23.4	0.17	36.0	0.17

Total volume of irradiation tube = 15 ml, *G/L* = Gas/liquid volume ratio; NTU = Nephelometric turbidity units.

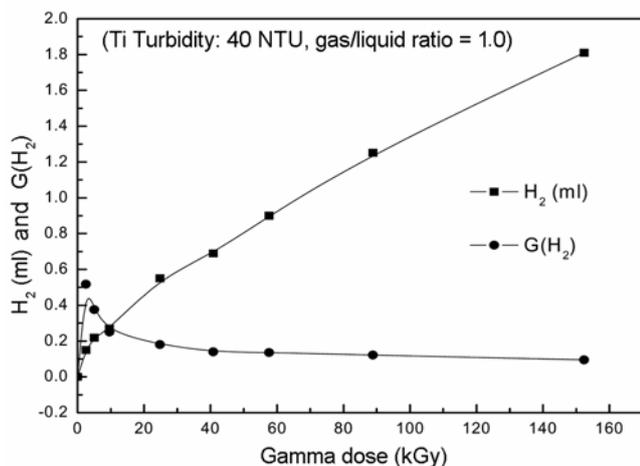


Figure 2. H₂ generation and G(H₂) as a function of absorbed dose (turbidity: 40 NTU, *G/L* = 1.0).

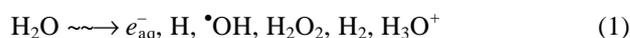
was sonicated for half an hour. The turbid mixture thus generated was filtered through a Whatman 540 filter paper and the filtrate was used for further experiments. The amount of turbidity was measured using ELICO Nephelometer (CL-52). A standard of 400 NTU turbidity was prepared by mixing 5 ml of 1% hydrazine sulphate, [(NH₂)₂H₂SO₄] with 5 ml of 10% hexamethyltetramine, (CH₂)₆N₄, and allowing it to stand for 24 h at room temperature and then diluting it to 100 ml. Calibration standards in the range of 2–10 NTU were prepared daily and the turbidity meter was calibrated before use. For characterization of Ti turbidity particles in the solution, the turbid solutions were evaporated to dryness under IR lamp, and Electron Spectroscopy for Chemical Analysis (ESCA) spectra and Transmission Electron Microscopy (TEM) images of the dried residue were recorded.

Ti concentration was measured by dissolving the turbidity in concentrated, HNO₃/HCl (5 ml acid + 20 ml turbid solution) and then analysing it by Inductively Coupled Plasma Mass Spectroscopy (ICPMS) technique.

Ti turbidity thus obtained was γ -irradiated using ⁶⁰Co-gamma source with dose rate of 60 Gy/min to 8.1 kGy dose in glass tubes. Before irradiation, the tubes were stoppered with a rubber septum and purged with Indian Oxygen Ltd AR (IOLAR) N₂ (<2 ppm O₂). The volume of the liquid and gas phases in the irradiation cell was varied to get the gas to liquid (*G/L*) volume ratio of 2.0,

1.0 and 0.5. H₂ produced on radiolysis of the samples and present in the gas phase was measured by gas chromatography using Porapak QS (2 m) column with Chemito-8510 gas chromatograph and thermal conductivity detector.

Radiolysis of water leads to the formation of following radicals and molecular products.



In the absence of any scavenger for free radicals, the molecular products will be destroyed by the following reactions in a closed system.



Thus, in a completely closed system, radiolytic decomposition of pure water is negligible². This is one of the reasons why water has been used as a moderator and coolant in nuclear reactors in addition to its low cost and abundance⁸. In the presence of millimolar concentrations of $\cdot\text{OH}$ radical scavengers and in open systems where gas can escape, the G(H₂) value (molecules of hydrogen formed per 100 eV of energy absorbed) can increase; which however, is not expected to exceed 0.45 molecules (100 eV)⁻¹.

The yield of radiolytic hydrogen generated was found to be proportional to the γ -dose. However, G(H₂) was found to increase initially with increasing γ -dose up to 5 kGy and thereafter it showed a decrease and was stabilized at a value of 0.2 at a dose of ~20 kGy. Maximum G(H₂) of 0.5 was observed at 5 kGy. For 40 NTU Ti turbidity and at gas to liquid volume ratio of 1.0, the variation in the H₂ yield and G(H₂) with γ -dose is shown in Figure 2.

Hydrogen gas was generated by radiolysis of aqueous solutions of Ti turbidity with gas to liquid volume ratio of 2.0, 1.0 and 0.5 and with γ -dose of 3.7, 7.4 and 11.1 kGy are shown in Table 1.

Increased hydrogen generation with increase in turbidity and γ -radiation dose is seen in this table. At high

dose and low G/L ratio, the observed apparent decrease in $G(H_2)$ value may be due to the increased combination reactions of $\cdot OH$ radical with H_2 (eq. (2)) as well as due to lowered probability of escape into gas phase. During irradiation, most energy is absorbed in the liquid phase. As we increase liquid volume, back reactions in liquid column predominate and lead to decrease in G value. As we lower the liquid volume, less energy is absorbed and thus the total volume of H_2 produced decreases. Hence, the gas to liquid volume (G/L) ratio for maximum H_2 generation has to be optimized. The G/L ratio of 1.0 was found to be optimum. Figure 3 shows H_2 produced and $G(H_2)$ as a function of L/G ratio for 3.7 kGy γ -dose and 20 NTU Ti turbidity.

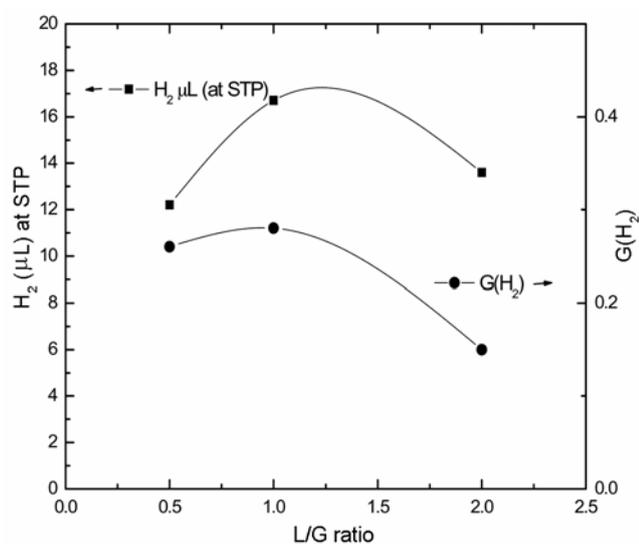


Figure 3. $G(H_2)$ and radiolytic H_2 produced at STP as a function of liquid/gas volume ratio (Ti turbidity: 20 NTU, γ -dose: 3.7 kGy).

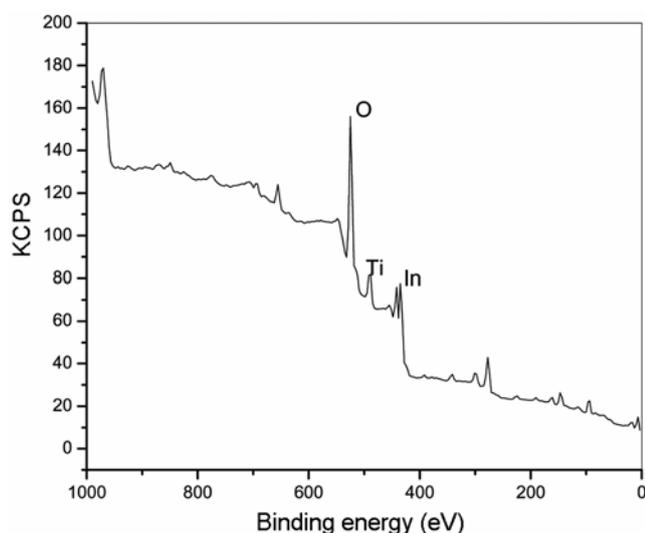


Figure 4. Wide scan photoelectron spectrum of the turbidity filtrate showing the presence of oxygen.

Ti turbidity will have Ti^{3+} ion, hydrated TiO_2 and possibly other Ti species in the solution. Figure 4 shows wide scan photoelectron spectrum (ESCA) of dried turbidity. Presence of oxygen peak indicates formation of titanium oxide species. As the dried turbidity powder was pasted on In (indium) foil for X-ray Photoelectron Spectroscopy (XPS) analysis, the signal of In was also seen in the wide spectrum. The concentration of Ti species will increase with the turbidity level. Total Ti concentration obtained after dissolution of turbidity as a function of turbidity is shown in Figure 5.

Ti^{3+} has high reactivity with $\cdot OH$ radicals ($1.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and intermediate reactivity with H-atoms and thus can interfere more efficiently with the recombination reactions; eqs (2) and (3), leading to more hydrogen generation¹⁰.



Possibility of Ti existing as hydroxylated or oxide species in turbid solution can also help in H_2 generation via semiconductor photolysis mechanism wherein some of the scattered γ -photon may be involved in the e^-/h^+ pair formation. For effective dissociation of water to produce H_2 , a few tens of eV to keV energy photons and e^- are required⁶. Turbidity may also play a role in attenuating γ -ray energy from MeV to keV/eV values resulting in H_2 production by photolysis. Figure 6 shows $G(H_2)$ as a function of Ti turbidity.

The energy of γ -rays is several times greater than that of UV photons and can generate electron hole pairs in the materials classified as insulators, such as metal oxides and metal hydroxides present in the turbid solution. An increase in hydrogen yield with an increasing amount of semiconductor powder suspension in water was observed in the study of hydrogen generation via e^-/h^+ pair formation

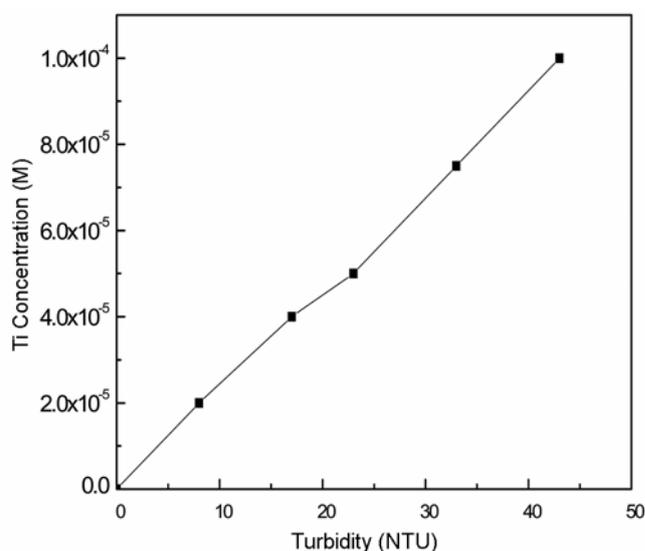


Figure 5. Ti concentration as a function of Ti turbidity.

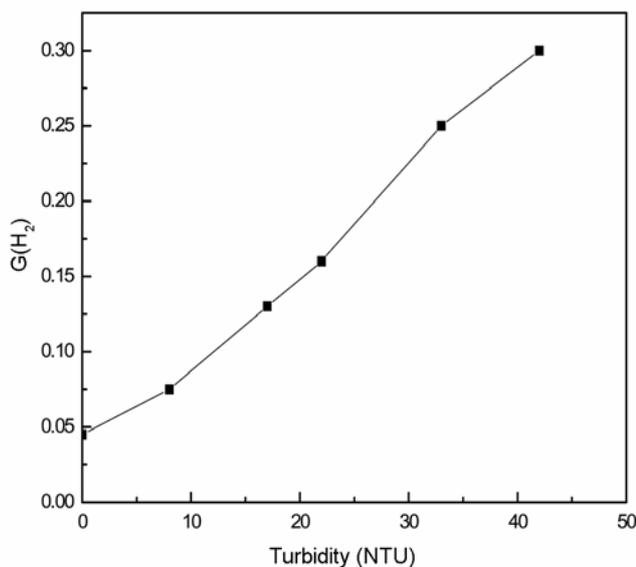


Figure 6. $G(\text{H}_2)$ as a function of Ti turbidity (γ -dose: 0.81 mega rads; $G/L = 2$).

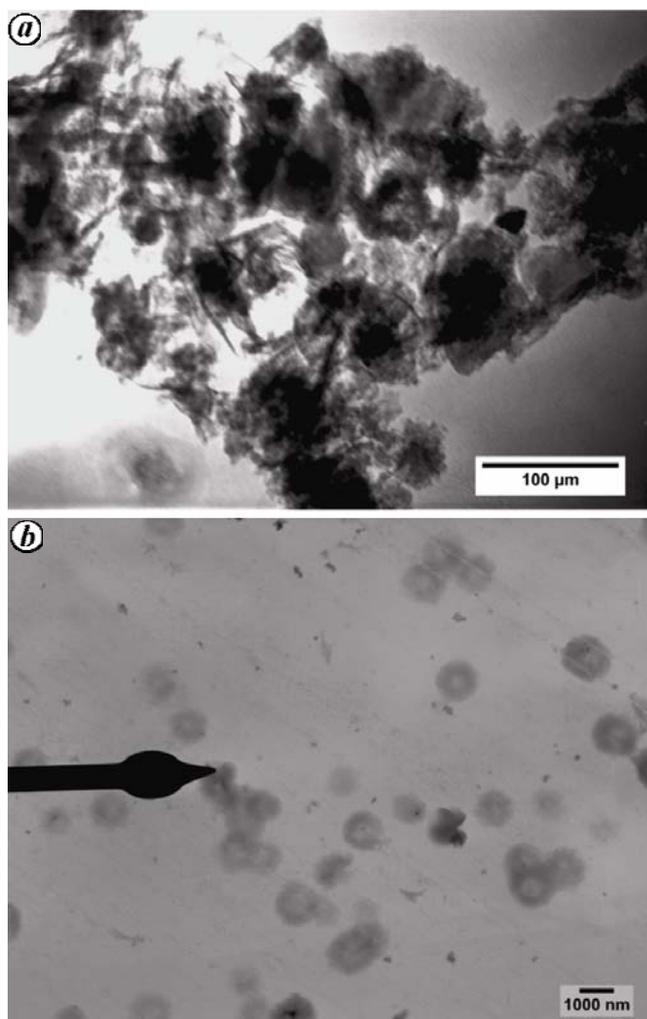
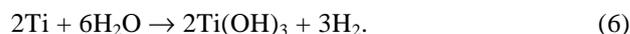


Figure 7. TEM of dried 70 NTU Ti turbidity: *a*, Un-irradiated; *b*, Irradiated for γ -dose of 22.3 mega rads.

and H_2 generation from electron liberated in the solution³. However, significant excess hydrogen generation or a regular relationship with an amount of oxide suspension was not observed for ZrO_2 , SrTiO_3 and BiTiO_3 (ref. 5). This also shows that in case any e^-/h^+ pair formation occurs due to γ -irradiation of turbidity particles, the e^- can get solvated in aqueous medium and lead to H_2 generation via reaction: $2e_{\text{aq}}^- \rightarrow \text{H}_2 + 2\text{OH}^-$. A plot of amount of TiO_2 nanoparticle ($\sim 2\text{--}5$ nm in size) versus measured $G(\text{H}_2)$ showed a saturation plateau for H_2 yield after 0.2% TiO_2 suspension; whereas, a continuous increase in hydrogen yield was observed as a function of the total absorbed dose⁴. This indicated that the main mechanism of H_2 generation is the radiolysis, and photocatalytic processes were of less significance as suggested earlier. The turbidity range and γ -dose used in our study is quite small compared to the literature value⁴ and hence our observations fall very well within the range of the linear part of the curve. Thus, any interference with the recombination reaction; eqs (2)–(4) leads to significant increase in $G(\text{H}_2)$ value as compared to other processes.

After γ -irradiation, turbidity samples showed decrease of Ti concentration in the solution (Table 2). The TEM micrographs of 70 NTU turbidity sample irradiated to 233 kGy and dried under IR, showed the formation of clusters with spherical particles of 10–40 nm; whereas with un-irradiated and dried turbidity irregular and larger size particles were formed (Figure 7). Formation of colloidal silver nanoparticles from silver solution with γ -irradiation is specified in literature¹¹. Metal oxides in colloidal or particulate form are normally insoluble in aqueous solution and can be dissolved by free radicals generated by radiolysis of water using them as one-electron reducing agents for dissolution¹² and can be again reduced to metals by solvated electrons coalescing to nanoparticle formation. In this case, Ti turbidity might have dissolved to some extent due to irradiation and leading to subsequent formation of Ti nanoparticles. This Ti can also lead to H_2 generation through the following chemical reaction with water.



Contribution in hydrogen generation by this reaction is minimal. Nanoparticles also provide larger surface area for enhanced photo-catalytic hydrogen generation.

As methanol (CH_3OH) is an efficient OH radical scavenger as well as a whole scavenger and its reaction with H and $\cdot\text{OH}$ radicals further helps in increased H_2 production¹³. The reaction and their rate constants are as follows.

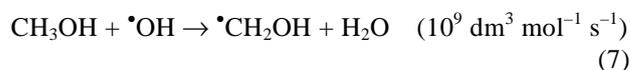
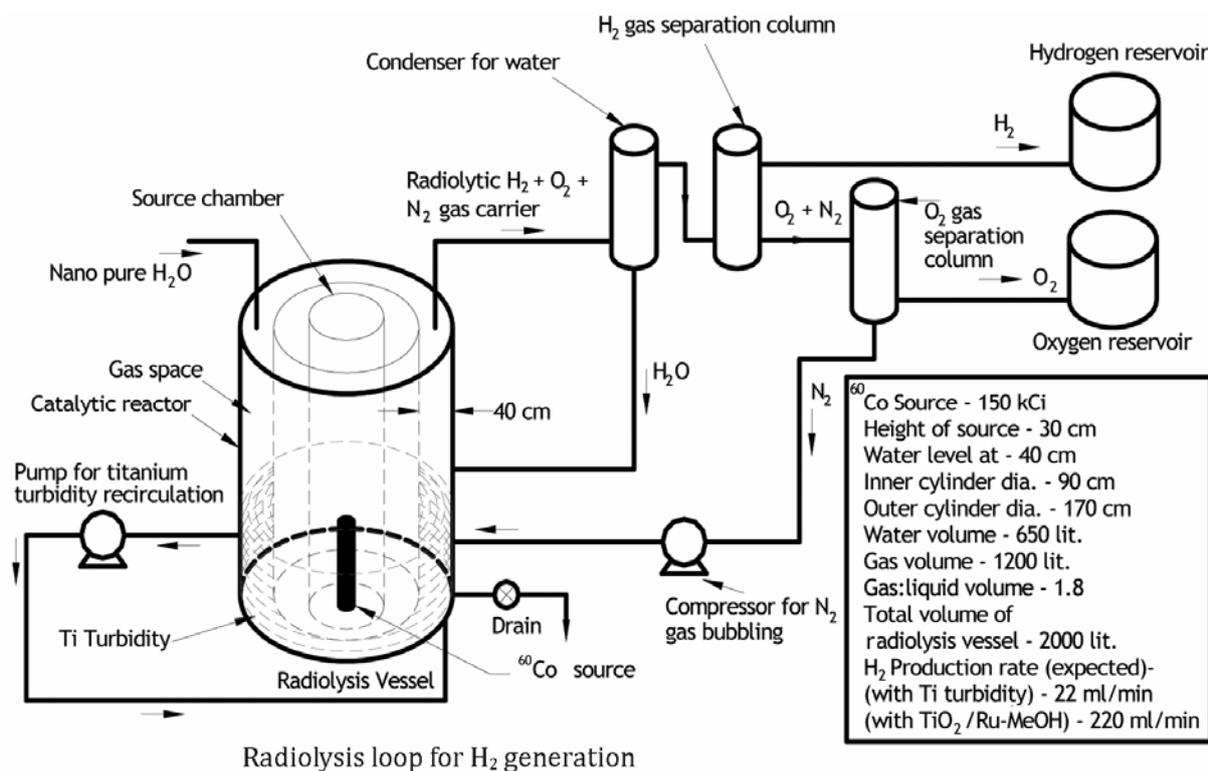
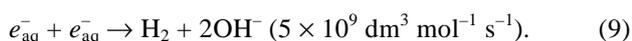


Table 2. Reduction of Ti concentration after irradiation

Ti turbidity NTU	γ -Dose (mega rads)	Titanium concentration (ppb)		Percentage of Ti reduction
		Non-irradiated	Irradiated	
35	7.0	71.2	22.7	68
52	17.3	450	156	65

**Figure 8.** Schematic of a test loop for the radiolytic H₂ production.

The hydrogen yield $G(\text{H}_2)$ of the aqueous methanol solution radiolysis is 2.4 as given here.

$$G(\text{H}_2) = G(\text{H}_2) + G(\text{H}) + 1/2G(e_{\text{aq}}^-) \quad (10)$$

$$2.5 = 0.45 + 0.55 + 1.4$$

Radiolysis of Ti turbidity containing 1.3 mol dm^3 methanol was performed. Addition of methanol increased the $G(\text{H}_2)$ value to 1.8. A hundred-fold enhancement in H₂ production by using radiolysis of Pt-doped TiO₂ and 2.46 mol dm^3 methanol is reported¹⁴. $G(\text{H}_2)$ of 1.05 is also reported for the $\dot{\gamma}$ -irradiation of TiO₂ nanoparticle suspension¹⁵.

With 150 kCi ⁶⁰Co γ source inside a test loop radiolysis of mixture of Ti turbidity (aqueous suspension of sub-micron size particles) and methanol mixture (~1.0–1.5 M), hydrogen generation at the rate 220 ml/min can

be achieved. A similar facility using TiO₂/Ru catalysed γ -radiolysis of water was also suggested earlier⁵. Thus, with the help of enhanced radiolysis of water in the presence of metal (Ti) turbidity and methanol by using γ -energy from the nuclear reactor core or nuclear waste, which otherwise, is hazardous to health, H₂ production at medium-scale level can be achieved. A schematic for such a facility is shown in Figure 8. This is similar to the added advantage of waste steam from nuclear reactors for producing desalinated potable water. This process does not involve handling of corrosive chemicals at high temperatures as required in thermal methods of H₂ generation by water splitting. The process also can be easily controlled with γ -exposure to the solution by manipulating height of ⁶⁰Co γ -source in the radiolysis vessel by lowering or raising it from the shielding chamber.

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MetPred: a web server for classification, identification and prediction of metalloproteases

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Metalloproteinases (MP) are a family of proteases which play a major role not only in normal physiological processes like normal turnover of extracellular matrix macromolecules but also in diseased conditions such as arthritis, cancer, brain disorders, skeletal dysplasias, coronary artery and heart disease. Members of the matrix metalloproteinases (MMP) family include MMPs, MT-MMP, ADAMs and ADAMTS. Majority of these proteins are drug targets with many of the MP drugs currently in trial phase. In the past, machine learning has been used to classify other proteins but no attempt has been made for classification of MPs. Realizing their importance, an attempt has been made to develop a support vector machine model to predict, classify and correlate major subclasses of MPs with their amino acid composition. The method was trained and tested on 229 proteins of MPs. The method discriminated MPs from other enzymes with Matthew's correlation coefficient of 1.00 and 100% accuracy. In classifying different subclasses of MPs with amino acid composition, an overall average accuracy of 98% was achieved. The performance of the method was evaluated using five-fold cross-validation. For understanding them in a better way, a web server MetPred has been developed for predicting MPs from its amino acid sequence at www.bifmanit.org/MetPred/.

Keywords: Metalloproteinases, support vector machine, web server.

METALLOPROTEINASES or metalloproteases (MPs) constitute a family of enzymes from the group of proteases, classified by the nature of the most prominent functional group in their active site. These are proteolytic enzymes whose catalytic mechanism involves a metal. Most MPs are zinc-dependent, some use cobalt. The metal ion is coordinated to the protein via three histidine imidazole ligands. The fourth coordination position is taken up by a labile water molecule¹. There are two subgroups of MPs: (i) exopeptidases: metalloexopeptidases (EC number: 3.4.17) and (ii) endopeptidases: metalloendopeptidases (3.4.24). Well-known metalloendopeptidases include: (i) matrix metalloproteinase (MMPs), (ii) a disintegrin and metalloproteinase (ADAM) proteins and (iii) a disintegrin and metalloproteinase with thrombospondin motifs

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