

Cobalt(II,III) Oxide - Manganese(IV) Oxide & Hydroxides Dissolution In Hydrogen Peroxide – Acetic Acid Solution

Syed Ahsan Imam[#]

[#]Process Engineer, Lotte Chemical Pakistan Limited

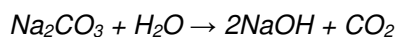
Based on Working Conducted During: Jan '19 – Oct '19

Abstract — Cobalt/Manganese based catalyst is recovered via precipitation through Soda Ash at certain pH. Various reactions occur during the process and undesirable oxides of Cobalt/Manganese are among them. These blackish solid result in deposition/filtration issues downstream. 3~5% Hydrogen Peroxide solution in 95% Acetic Acid is proven to be effective in dissolving these. This writing encompasses merely on the in-house conducted experiments followed by implementation.

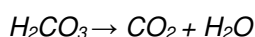
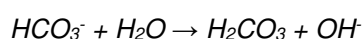
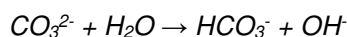
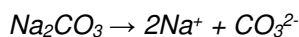
I. FORMATION OF Co/Mn PRECIPITATES ALONG WITH OXIDES

With addition of 20% to 30% soda ash solution, soluble metals i.e. Co/Mn (mainly in the form of acetates) convert into insoluble carbonates which are filterable. However, various side reactions also propagate along with. In this section, involved possible reactions will be covered.

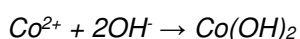
One of the least worried reaction is the acid-base (primarily) followed by dehydration when soda ash combines with water. This reaction is generally unfavorable. This is because sodium hydroxide is relatively unstable and reacts with atmospheric carbon dioxide to form carbonic acid. This can be verified by placing caustic in an open beaker and measuring pH where the pH will be dropped gradually due to aforesaid phenomenon.



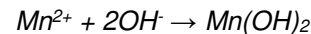
Actually, soda ash breaks up into respective ions and eventually forms carbonic acid which in fact doesn't dissociate further due to its weak acid properties. The formation of carbonic acid is not much significant unless the system gets rich with carbon dioxide which in our case is not possible due to atmospheric conditions however minor transformation is somewhat inevitable.



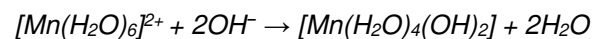
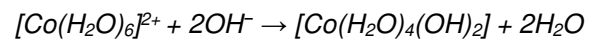
This hydroxide ion has the potential to react with Cobalt and forms Cobalt Hydroxide which is a pink solid and is not considered troublesome.



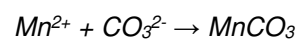
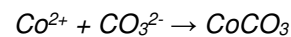
Reaction involving conversion of Manganese into Manganese Hydroxide is also possible however, it is to be noted that, this is a white solid/pale pink and highly susceptible to oxidation upon contacting with air and becomes darker in color.



Various publications also suggest that, Cobalt and Manganese also forms neutral complexes upon reacting with hydroxides which are insoluble in water. Hexaaquacobalt(II) ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and Hexaaquamanganese(II) ion $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ are the simplest ones that form. For Cobalt, it is pinkish however for manganese, it is pale pink but turns darkish (brown possibly) upon interacting with oxygen.



Since the system is dosed with sodium carbonate therefore Cobalt and Manganese form basic carbonate precipitates as well which is again insoluble in water. This is the preferable precipitate.



All the said reactions occur in a vessel where pH is maintained between 8~9.5 to ensure excess basic environment. It was observed that, additional complex/compounds form involving oxides i.e. Cobalt (I,II) Oxide (Co_3O_4) and Manganese(IV) Oxide (MnO_2) which are blackish in appearance and trouble maker because of finer particle size and deposition tendency. They are favorable to form under two known circumstances:

- High pH operation involving excess soda ash solution.
- High residence time.

For point (b), it was noted that, if precipitated solution having normal pH of 8~9.5 is kept under atmospheric condition for some time then it will turn darker i.e. brownish to blackish. One of the reasons is already aforementioned regarding Mn hydroxide complexes which are unstable and undergoes oxidation and it is suspected that same phenomenon also applies for Cobalt hydroxide complexes as well.

For point (a), the precipitation theory suggests reaction competition between carbonates and hydroxides. Since,

carbonates are always preferred which appears to be optimally formed under pH ranges of 8~9.5. Above that number, it is estimated that hydroxide tends to form more which can in turn result in darker solution. It is to be noted that, these are well understood for the formation of hydroxide complexes. For oxides i.e. Cobalt (I,II) Oxide (Co₃O₄) and Manganese(IV) Oxide (MnO₂), these are usually formed under similar conditions or may form after dissociation of various complexes.

It is to be noted that, in literature there is an ambiguity about the darker brown/blackish compound. It is most commonly quoted as Mn₂O₃.xH₂O. However, some sources quote it as a hydrated Manganese(IV) oxide, MnO₂.xH₂O which we have already discussed earlier.

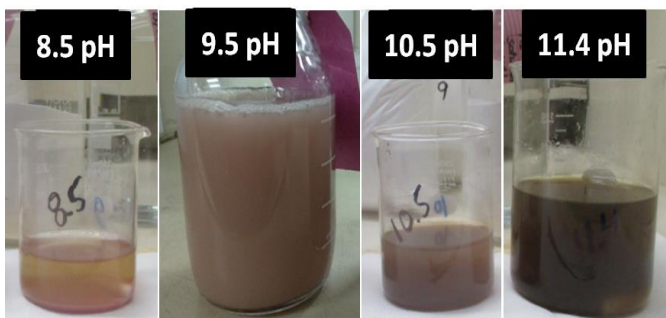
II. PICTORIAL ILLUSTRATION OF pH IMPACT / RESIDENCE TIME

Below is the pictorial example of two samples having same pH of ~9. The pink one is taken under normal running condition with stable maintained pH while the second sample was taken from the same source during which the precipitated solution was retained for some time (giving it higher residence time).

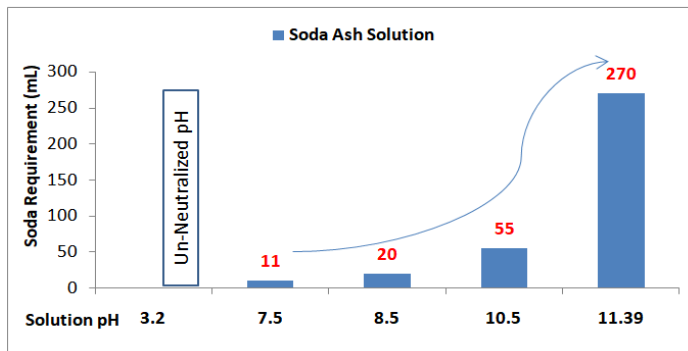


Below is the pictorial example of various samples that were prepared in laboratory by adding soda ash in order to prepare samples of different pH followed by giving some residence time. It can be noted that sample with high pH turns more blackish as compared to their counterparts. The darkness grading is:

(less dark) 8.5 > 9.5 > 10.5 > 11.4 (most dark)

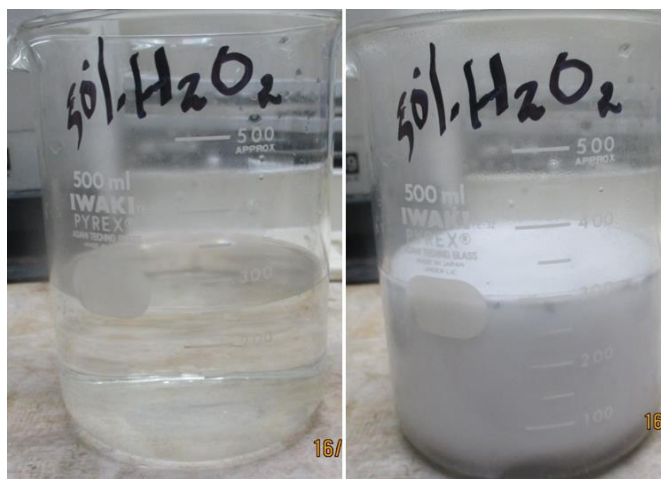
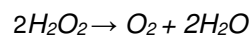


It was also noted that soda ash solution requirement increases steeply as we intend to increase its pH i.e. to change pH from 8.5 to 10.5 we need to add soda ash solution 2.75 times for what we had earlier dosed and vice versa. The high noticeable change is when pH is increased to 11.4 where the requirement increased by at least 4.9 times. This illustrates that significance of pH control with reference to soda ash consumption as well as the enrichment of hydroxides and oxides.



III. DISSOLUTION OF OXIDES/HYDROXIDES THROUGH H₂O₂/AA SOLUTION

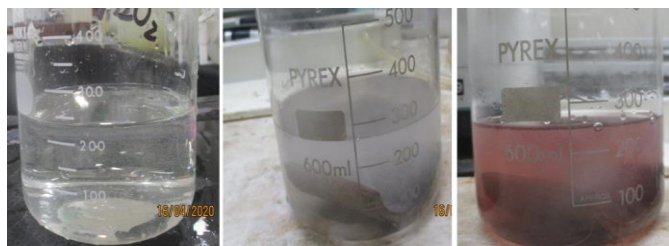
Commercial grade (50%) H₂O₂ is highly reactive and possess strong oxidizing specification. Itself, it is unstable and decomposes to form Water and Oxygen especially under the presence of metals. This is an example of disproportionation reaction where oxidation state of oxygen changes from -1 in H₂O₂ to -2 in H₂O and to 0 in O₂. This is why it results in exothermic reaction and oxygen bubbles out from solution.



This is a 50% H₂O₂ solution as received. As soon as metal piece containing Co/Mn layer was put into it, vigorous reaction started and sample color turned into cloudy white with fumes coming out from the surface top. This is undesirable as it results in loss of H₂O₂.

In acidic media, it is powerful agent for removal of various depositions. However, strength and temperature control must be established to avoid high exothermic reaction.

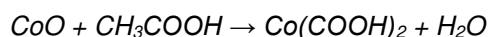
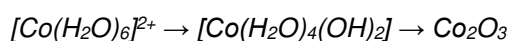
Below picture illustrates the example of 3% H₂O₂ solution Acetic Acid. It can be seen that relatively less vigorous reaction was observed. The sample initially turned turbid later changed its state to pinkish/reddish indicating dissolution of Co/Mn precipitates. This is an example of controlling disassociation of H₂O₂.



In Acetic Acid (95%), Hydrogen Peroxide usually forms Peracetic Acid which is an equilibrium (reversible) reaction and the exact extent of formation is debatable. The intent of using Acetic Acid is to control the reaction as well as to act as a mobile phase for dissolution because using 50% H₂O₂ results in explosive mixture upon contacting Co/Mn compounds. Secondly, these oxides are not much soluble in Acetic Acid specifically.



The major action of Hydrogen Peroxide is the change of Cobalt/Manganese oxidation state i.e. +2 to +3. Many sources explain that the change is merely as mentioned below while some suggests as to be CoO(OH) Cobalt Hydroxide Oxide. However, one thing is clear that the resultant solution is dark brown/blackish precipitate. Reaction between CoO and Acetic Acid is also reported but the basis is conjecture.



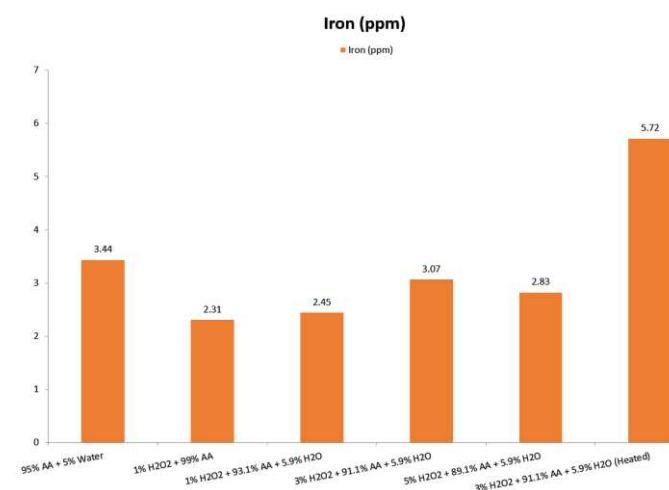
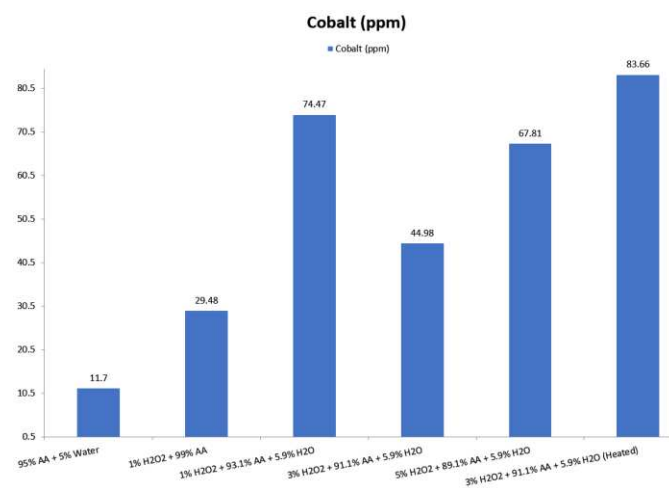
Here, it is to be noted that CoO or Co(II)O is itself dark green which often appears purplish and is the result of Co(OH)₂ dehydration. Below is the pictorial illustration of ~4% Hydrogen Peroxide solution in Acetic Acid after contacting/dissolving Cobalt Manganese oxides which turns from transparent/pale blue to dark brown/red and later samples revealed changes to purplish/blackish.



IV. LAB EXPERIMENT RESULTS

Different strength of Hydrogen Peroxide solution were prepared in Acetic Acid to observe the efficiency of dissolving Co/Mn oxides and 3% solution was selected among them. The extraction of Co was also on higher side however, being a corrosive agent, Iron loss from metal sample was also evident. Analysis details are attached in a separate annexure at the end of this document.

The experiment was conducted at room temperature however;



the heated solution experiment was between 80~85 deg C. One thing to be noted that, 1% H₂O₂ + 93.1% AA + 5.9% H₂O solution resultant Cobalt (post-soaking) was also on higher side however, the results were not so promising when similar experiment was conducted at aforementioned temperature.

V. DISSOLUTION OF METALS IMPACT

Cobalt/Manganese based catalyst is recovered via precipitation through Soda Ash at certain pH in an atmospheric vessel. To optimize reaction rate 70~75 deg C temp is usually maintained. Various reactions occur during the process and undesirable oxides of Cobalt/Manganese are among them. The formation increases exponentially in the presence of caustic soda.

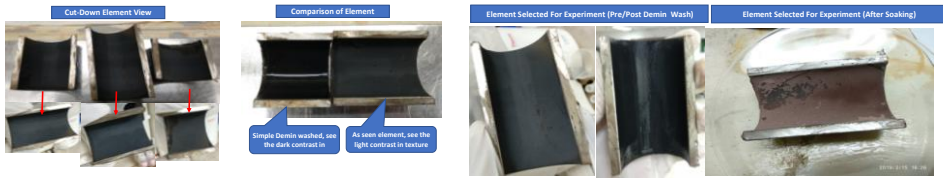
These blackish solid result in deposition/filtration issues. Based on the aforementioned experiment, a vessel which was coated with these undesirable oxides were successfully cleaned as can be seen from the below attached pictorial comparison.



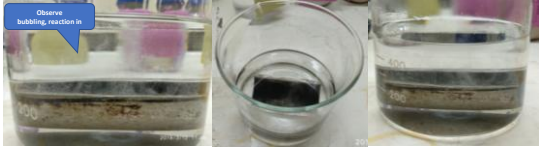
VI. REFERENCES

- [1] Recovery of Co/Mn from ash of residue from manufacture of TMA by acid extraction – 1981 – Harper, Pietsch
- [2] Peroxy Compounds – Ullmann's Ency. Of Ind Chemistry
- [3] Peracetic acid – Rao, Mohan - IICT, India
- [4] Preparation of Peracetic Acid from Acetic Acid and Hydrogen Peroxide: Experimentation and Modeling – Feb '18 – Zhao, Liu
- [5] Petrucci, Ralph H. (2007). General Chemistry: Principles & Modern Applications
- [6] Et.al

	AA Solution	1% H2O2 Solution in Glacial AA	1% H2O2 Solution in AA	3% H2O2 Solution in AA	5% H2O2 Solution in AA	3% H2O2 Solution in AA (Temp)
Temperature (Degree C)	Ambient	Ambient	Ambient	Ambient	Ambient	75 ~ 80
Total Volume (ml)	400	500	450	450	450	400
AA Volume (ml)	400	495	445.5	436.5	427.5	388
H2O2 Volume (ml)	-	5	4.5	13.5	22.5	12
H2O2 Mass (Kg)	-	0.00575	0.005175	0.015525	0.025875	0.0138
AA Mass (Kg)	0.42	0.51975	0.467775	0.458325	0.448875	0.4074
wt/wt Solution (%)	-	1.094%	1.094%	3.276%	5.450%	3.276%
Soaking Period (hrs)	3	3	3	3	3	1
Cobalt (ppm)	11.7	29.48	74.47	44.98	67.81	83.66
Nickel (ppm)	3.44	2.31	2.45	3.07	2.83	5.72
Chromium (ppm)	-	-	0.72	0.88	0.74	-
Filter Element (Before Soaking)						
Filter Element (After Soaking)						
Filter Element (During Soaking)						
Residue Solution						

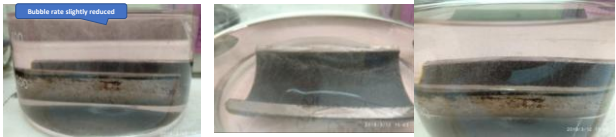


Element Soaking In H2O2 Solution (Initial Appearance)



3% H2O2 Solution was prepared in DI Solvent. Total Volume: 500 ml. H2O2 Volume: 15 ml.

Element Soaking In H2O2 Solution (After 4 hrs Soaking)



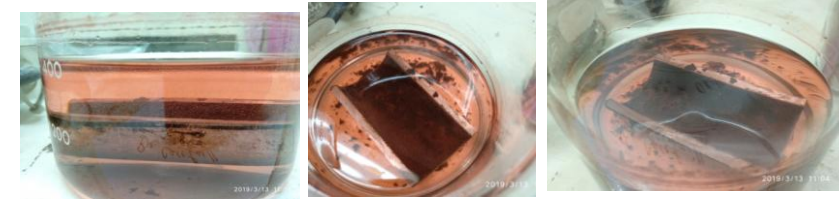
No change in level was observed, color changed to slight pinkish, bubbling rate reduced

Element Soaking In H2O2 Solution (After 22 hrs Soaking)



100 mL level dropped. Bubbling rate became zero. Color changed to dark pinkish. Some cleaning observed.

Element Soaking In H2O2 Solution (After 22 hrs Soaking)



15 ml H2O2 Solution was added. Bubbling rate started. Peeling off material was observed.

Element Soaking In H2O2 Solution (After 32.5 hrs Soaking)



Bubbling rate stopped. Level dropped to 370 ml approx. Again 15 ml H2O2 solution was added.

Element Soaking In H2O2 Solution (After 56.5 hrs Soaking)



Bubbling rate stopped. Level dropped to 300 ml approx.

Residual Solution

