

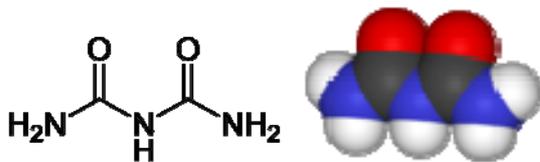
Plant Manager +

This is the second in a series of discussions from a selection of round table topics discussed on the UreaKnowHow.com website. UreaKnowHow.com promotes the exchange of technical information to improve the performance and safety of urea plants. A wide range of round table discussions take place in the field of process design, operations, mechanical issues, maintenance, inspection, safety, environmental concerns, and product quality for urea, ammonia, nitric acid and other fertilizers. For more information please visit www.ureaknowhow.com.

The second subject to be discussed is the problem of high biuret content in the urea product at lower plant loads.

Problem No. 2 High Biuret level at low plant loads

Biuret is formed from urea according to the following overall reaction: $2 \text{ Urea} \rightleftharpoons \text{Biuret} + \text{NH}_3$. In fact this reaction proceeds in three steps: When heating a concentrated urea solution in water or a urea melt, urea is present in two forms, a keto and an enol form. The enol form of urea primarily decomposes into NH_3 and HNCO (cyanic acid). Cyanic acid reacts with another urea to biuret.



The Biuret molecule in 2D and 3D view.

All these reactions are equilibrium reactions. The biuret formation according to these reactions is favored by higher residence times, higher temperatures and lower ammonia partial pressures. Biuret is considered an impurity in urea when used as a fertilizer as it has been identified as injurious to citrus foliage and to certain germinating seeds, but which biuret level really causes damage to the plants is disputable. The earliest urea plant designs produced urea with up to 5 wt% biuret. From 1955 to present, many urea plants were designed to produce low-biuret product with not more than 0.3 wt% biuret by means of a crystallization section. The lower biuret concentration was found to be safe for these special applications which amount to about two percent of total urea fertilizer consumption.

Modern plant designs are successful in producing urea prills and granules with 0.8 wt% biuret. These plants can handle 98 percent of the urea market with simpler and more cost-effective urea finishing designs that produce higher quality products with better storage and handling characteristics.



Mr. Mohammed Al-Jeshi of Safco in Saudi Arabia posts an interesting operational question:

What is the relation between Plant load & Biuret content in the final product?
Any ready chart available ?

Mr. B.P. Suresh of Nagarjuna Fertilizer and Chemicals Limited in Kakinada, India replies following:

Biuret formation depends only on temperature and residence time. There is a relation between plant load and biuret formation with respect to residence time. In case of increase in load, the residence time will come down and biuret formation will also come down.

Mr. Mark Brouwer of UreaKnowHow.com in the Netherlands asks for some more specific information:

Anybody has a graph available derived from practical experience: so biuret in product versus plant load ?

Or what is your biuret level at 60% plant load ?

Further I like to know what are the "tricks" to reduce the biuret formation at low plant loads ?

Mr. Waqqar Ahmed of Fauji Fertilizer Corporation in Pakistan replies with several valuable suggestions:

At reduced load biuret can be controlled by following measures.

- 1- Keep urea solution levels in holders as low as possible i.e. MP/LP/vacuum section.
- 2- Keep NH_3/CO_2 ratio slightly on higher side.
- 3- Maintain urea stripper temperature ~ 198-200°C for Snamprogetti technology.
- 4- For plants using prill tower, urea melt delivery line to the prill tower is normally jacketed with low pressure steam, here urea melt gets both residence time & temperature, reduce jacketing steam in this line in case of low load operation.
- 5- If dust solution recovery is ongoing reduce its flow rate.

Mr. Ahmed continues ...

Max allowable limit of biuret in the final product is set 1.0 wt% at our plant.

In normal operating conditions biuret is maintained < 0.9 wt%, however at low load operation it sometimes exceeds 0.9 wt% but remains less than set limit.

If biuret content exceeds the allowable limit, shipment of product is stopped & urea is stored in bulk storage, from where it is recovered again in the form of solution.

Mr. Mohammad Rastegaryan of PIDEMCO, Iran asks for some clarification:

What does solution mean? Do you mean in the form of solution?

If so it is possible to add onspec urea in order to reduce Bi content in urea storage.

Mr. Ahmed replies:

Off spec product due to moisture, biuret, prill shape, fines etc is diverted in bulk store (separate from on-spec stored urea). From off spec piles urea solution of ~ 70-80 wt% concentration is prepared to recycle back to the vacuum section.

Mr. Rastegaryan suggests another solution to handle off spec product:

You are right. but sometimes you can pour fresh and on spec urea (directly from plant) via tripper over off spec product in the bulk storage until acceptable range. In addition when it is transferred to bagging system it will be mixed better.

Mr. Muhammad Adnan Hanif of Fauji Fertilizer Corporation in Pakistan adds his experiences to the discussion:

I agree with you the off spec urea may be mixed with on spec urea in such a proportion that your mixed product remains in the specified limits.

Recycling of off spec urea through dissolving in water and then again passing it through processing units like vacuum and prilling section will be not a good solution in term of product quality [as biuret will again increase] and energy utilization in term of steam at vacuum section will also increase.

Then Mr. Al-Jeshi who started the discussions originally comes back and gives the background of his initial question. He wants to influence the biuret level in the final urea product as he likes to operate the urea plant at a lower load due to a shut down of one of the ammonia plants.

I understand that Biuret can be controlled in a Snamprogetti process by increasing the NH_3/CO_2 ratio. What modifications can be considered in a Stamicarbon process (CO_2 stripping) to control the product quality ?

We have one ammonia plant S/D and want to utilize all excess CO_2 from another ammonia plant to maximize our urea production. Unfortunately, product quality expected to be off spec with respect to Biuret in case our urea plant will be operated at 70% load.

Mr. Majid Mohammadian of PIDEMCO in Iran replies with several suggestions and a question:

As you know in a urea plant biuret formation is caused by two factors: one is residence time and the other is temperature.

So I have following suggestions:

- 1-Confirmation about the level measurement in urea solution tank, evaporators, rectifier, H.P stripper, level tank of rectifier outlet and suction of the melt pump and maintaining these as low as possible.
- 2-Minimum recommended temperature in areas with higher than 50 wt% urea concentration.
- 3-Higher N/C ratio if possible
- 4-Higher capacity if possible

At 70% plant capacity how much is your biuret content ?

Mr. José Azócar of Fertinitro, Venezuela introduces another problem related to biuret levels:

At present we are having results of biuret content in the final product above 0.9 wt%, in one of our units, even when the load of the plant is 100%; we have tried to reduce this content doing all the recommended procedures (lowing the level of the decomposers holders, lowing the temperature of the high pressure stripper and etc.). We have considered taking sample in several points in both units to figure out what is the difference between them. My question is: is there any other procedure to consider in order to reduce the biuret content?

Mr. Prabhat Srivastava of TATA Chemicals Limited in India shares his valuable experience:

Almost all possible causes of formation of Biuret have been covered.

No matter which is the technology of urea, biuret increases with increase of urea concentration, high temperature and residence time.

Through co-relation, with process temperature and biuret, it is clear that temperature has significant impact on the biuret formation. Other than this if we run plant load at low capacity and maintain same operational parameters which we maintain at high plant load, than the residence time increases because of low flow velocities in comparison to a high plant load.

And another case: if one recycles melt urea (which has already a high biuret concentration) than this will give impact on the biuret levels in the final product. To avoid this if plant load is low than optimize the process temperatures in HP/MP and LP and maintain low levels where ever it is possible. In the same way in vacuum and pre-vacuum section where rate of biuret formation is very high due to concentration, level can be kept at a lower side. An optimized rate of recovery can be lined up at low plant load.

Mr. Sam Q. Raman of Fertco in India introduces another interesting cause for biuret formation and provides also valuable suggestions to reduce biuret levels at lower plant loads:

Check the urea melt pump efficiency: If you have lower efficiency you will have higher temperature difference between Evaporator and discharge temperature at prill tower top.

You can think of having two parallel melt lines to Prill tower. Reduced size line can be used for low load to increase the velocity.

Import urea solution from other plants (if you have second train of Urea plant)

For a temporary load reduction still the best option is to store it as off spec product and mix it with on spec product in proper proportion

Mr. Brouwer of UreaKnowHow.com in the Netherlands adds to it:

Also check temperature of steam heating of melt lines, melt temperature at prilling bucket should be minimum to have minimum biuret.

But biuret also increases crushing strength ! Anybody knows/sees any difference in crushing strength in 0.8 wt% biuret prills and 1 wt% biuret prills ?