

Development of Indigenous Source of Cobalt Suitable for Radiation Technology Applications

Bhaskar Paul and A.K. Sharma

Materials Processing Division

and

M.F. Fonseca, R. Sadanandam and A.C. Bidaye

Former Colleagues at Materials Processing Division

and

K. Srikant

Metallic Fuels Division

Abstract

The present article highlights the developments made in the field of indigenization of the technology for preparation of cobalt shapes for radioisotope applications from a secondary resource. In the first step, the process of extraction of cobalt in the form of metal powder from a secondary indigenous resource as spent ammonia cracker catalyst is described. In the second step, the processes of conversion of cobalt metal powder into the desired shapes followed by coating over the finished products have been presented.

Introduction

The role of Cobalt-60 as a radiation source in teletherapy for the treatment of cancer needs hardly to be reiterated. Although not used commonly in developed countries, cobalt-60 teletherapy machines can still be regarded as a very viable and cost effective option for the treatment of a sizeable fraction of cancer patients. At present in India, there are only 399 teletherapy units (280 telecobalt units and 119 linacs). As per the IAEA advisory group criteria, it is estimated that more than 1000 teletherapy units will be required in the near future. Considering the large requirements of teletherapy, BARC has designed and developed an advanced telecobalt unit, which was named as Bhabhatron-II. While the success of Bhabhatron-II "lives" at the interface between many disciplines, its dependence on cobalt-60 source is arguably the strongest. The Board of Radiation and Isotope Technology (BRIT) fabricates and supplies 10 to 15 high intensity cobalt-60 sources to cancer hospitals annually for use in cobalt-60 teletherapy units. High specific activity (up to 320 Ci/g) ^{60}Co pellets required for teletherapy is normally imported by BRIT.

High specific activity cobalt-60 sources are required for both imported and indigenous teletherapy machines

(BRIT has been supplying them, mostly using imported cobalt-60), while the development and launch of indigenous system Bhabhatron-II warrants further impetus to ensure sustainable indigenous sourcing of both high sp activity cobalt-60 and raw material for cobalt targets for irradiation.

^{60}Co required for the fabrication of sources is produced in nuclear power reactors by the following nuclear reaction: $^{59}\text{Co} (n,\gamma) \rightarrow ^{60}\text{Co}$. Cobalt metal (^{59}Co) is loaded in adjustor rods in the form of nickel-plated cobalt pellets with the following dimensions: 1 mm diameter and 1 mm height. The activity induced depends on the duration of irradiation to the neutron flux in the reactor. The adjustor rods from the power reactors are then transported to the cobalt handling facility and then cut under water.

There are also other special NDT applications (e.g. in DAE Units; ISRO etc) requiring very high intensity Cobalt-60 (several hundred curie) for radiography (cf. conventional strength radiography cameras of Ir-192 and Co-60) and the sources for them need to be of very high specific activity comparable to that of sources for teletherapy. This requirement could also be met using the combination of indigenous raw material cobalt and irradiation in NPPs

operating at high capacity factors. For these application nickel-plated cobalt pellets of 6 mm dia. x 25 mm height are activated in a nuclear reactor.

Among the main factors contributing to the activation of cobalt in reactor, the shape and size of cobalt pellets is important. The shape and size are important because irradiation time greatly depends on surface area of the material being exposed to radiation; smaller the material size, larger the surface area per unit mass and faster the irradiation. The important physical properties that are required for the pellets are its sintered density & dimensional accuracy. Sourcing cobalt raw material and manufacture of right size and shapes achieved by BARC adds greater strength to the indigenization efforts in a holistic manner.

India is one of the very few producers of large-scale industrial sources of cobalt-60 (typical sp acty 100 Ci/g; e.g. for industrial gamma plants) in the world. Thanks to our NPPs operating at high capacity factor over the past 4-5 years, the scope to produce cobalt-60 of much higher specific activity - upwards of 160-180 Ci/g, with potential to go above 200 Ci/g, and suitable for making teletherapy sources - gives India (BRIT, NPCIL, BARC) unique advantage to become self-reliant in the field of cobalt-60 in near future.

BRIT is in a position to access cobalt raw materials from direct import or through local agents. However, due

to enforcement of technology control regimes, there is an uncertainty in their import. In addition, cobalt is a metal of strategic importance, neither primary resources of cobalt exist nor does indigenous large scale cobalt metal production exist. Therefore, all possible secondary resources of cobalt need to be explored to establish indigenous technology for the production of cobalt shapes for radio-isotope applications.

Materials Processing Division has investigated in detail some of these secondary resources like Alnico scrap, copper converter slag, beta cake from the zinc industry, deep sea nodules and spent ammonia cracker catalyst (SACC)¹⁻⁴. The last among these i.e, SACC, is interesting, since it is produced within DAE in large quantities as waste. The catalyst in the form of pellets is used to crack ammonia (for producing H₂ in-situ). On long use, the catalyst pellets degrade, whereby they are no longer suitable for usage and are discarded. This discarded material can be procured from HWB (Thal, Maharashtra).

The Process

i) Extraction of cobalt from spent catalyst

The entire process for extracting cobalt from the spent catalyst and its conversion to cobalt powder and finally to nickel plated shapes of the specified shapes is depicted in the flow-sheet Fig. 1.

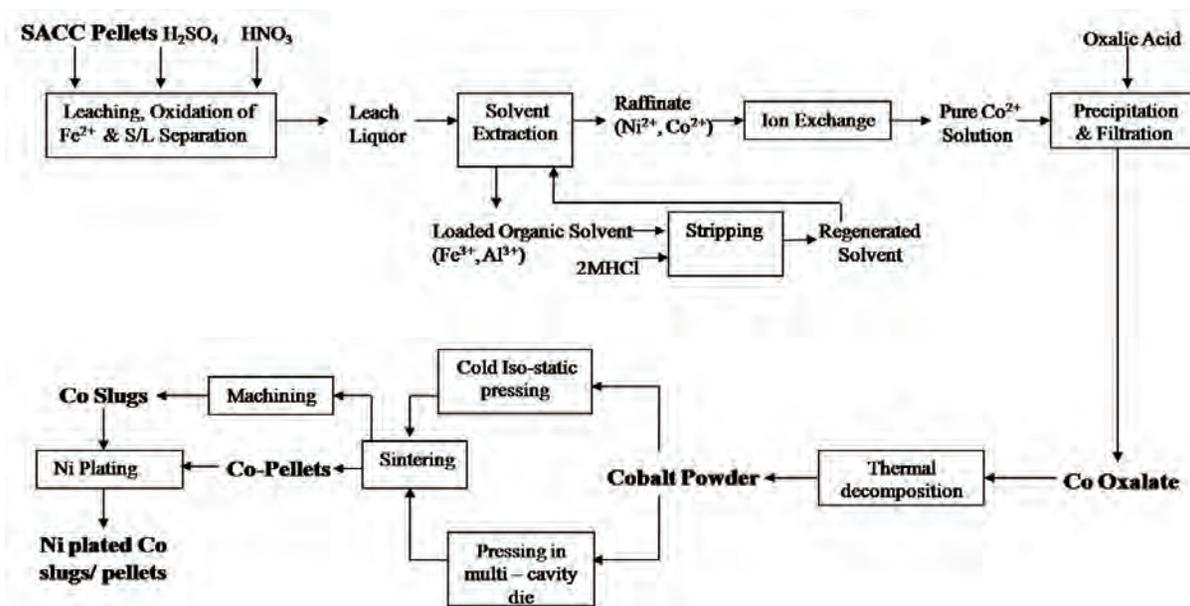


Fig. 1 : Flow sheet for extraction of Co from spent catalyst and conversion to required shapes.

The SACC catalyst pellets were analysed and the typical composition is reported (Fig 2). The as-received pellets dissolve easily in 2M H_2SO_4 at 60-80°C without any pretreatment/communion. A typical batch for processing these pellets involves 15 kg of catalyst pellets in 100 L Teflon lined stirred vessel. After leaching, Fe^{2+} is oxidized to Fe^{3+} with a slight excess (to stoichiometry) concentrated nitric acid. Subsequently, a suitable S/L separation is used before solvent extraction (SX).



Fig. 2: SACC Pellets and their composition

Constituent	Weight%
Al ₂ O ₃	36.5
Fe ₂ O ₃	31.5
CoO	29.5
NiO	0.27
K ₂ O	0.70
Binder	1.53

SX using counter-current mixer-settlers is employed to separate Fe^{3+} and Al^{3+} from the oxidized leach liquor. The solvent used to achieve this consists of a mixture of 85% saponified 0.5M D2EHPA and 0.7M TBP in n-dodecane using 4 stages each for extraction and stripping. Stripping is carried out using 2M HCl. The raffinate is passed through an activated carbon column to make it free of any entrained/dissolved organic before ion exchange (IX).

SX raffinate, so obtained from the above treatment consists of essentially cobalt with a small nickel impurity. In order to remove this Ni, the solution (pH adjusted to ~3.0) is passed through an ion exchange resin bed consisting of Dowex M4195 resin beads.

Pre-conditioned resin partially fills the acrylic columns. Ni elution is facilitated with 0.25 M H_2SO_4 , whereby the eluate is discarded after a suitable treatment.

The product solution obtained after ion exchange has a pH of ~3.0 which is adjusted to 3.5 - 4.0 using 12.5M NaOH solution. A slight excess (over stoichiometry) of oxalic acid is added in order to precipitate cobalt as its oxalate salt. The pure solid is filtered using a nutsche filter which is then washed with sufficient quantity of DM water. Then it is dried at 110- 120oC to constant weight to obtain the desired intermediate product, cobalt oxalate (Fig. 3), which is sent for further downstream processing.



Fig. 3: Cobalt oxalate

ii) Conversion of cobalt oxalate to desired metallic shapes

Pure cobalt powder (Fig. 4) is obtained from thermal decomposition of cobalt oxalate at elevated temperatures under a reducing atmosphere of argon-4% hydrogen gas mixture in a specially designed decomposition reactor.



Fig. 4: Cobalt powder

While the decomposition of cobalt oxalate begins at around 350°C as revealed by TG/DTA analysis (Fig. 5), the cobalt metal powder produced at this temperature is unstable and highly pyrophoric in nature and difficult to handle. The heating (and cooling) schedule of the oxalate has been optimized to yield cobalt powder with good flowability as well as sinterability. The SEM images of the cobalt oxalate and metal powder are shown in Fig. 6.

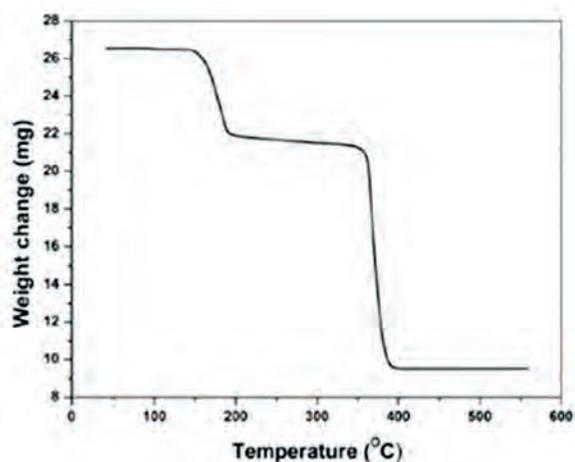


Fig. 5: TG plot for decomposition of cobalt oxalate to cobalt powder

Good flowability and sinterability of the cobalt powder are needed because in the next step the powder is to be filled into silicone rubber moulds for making cobalt slugs or into a multi-cavity die having 100 holes of 1.2 mm dia. for making pellets. The rubber moulds are compacted at 250 MPa in a Cold Isostatic Press, while a bi-directional hydraulic press is used for compacting the powder to make pellets. The green compacts so obtained are sintered in a sintering furnace at 1300°C under reducing atmosphere. Process parameters like compaction pressure, sintering temperature and holding time for green cobalt pellets have been optimized for getting sintered density of more than 98% of theoretical density.

iii.) Ni Plating over final shapes

The radioactive cobalt slugs and pellets have to be shielded from the external environment and this is achieved by covering them with a layer of nickel. Two barrel plating facilities one for cobalt slugs with

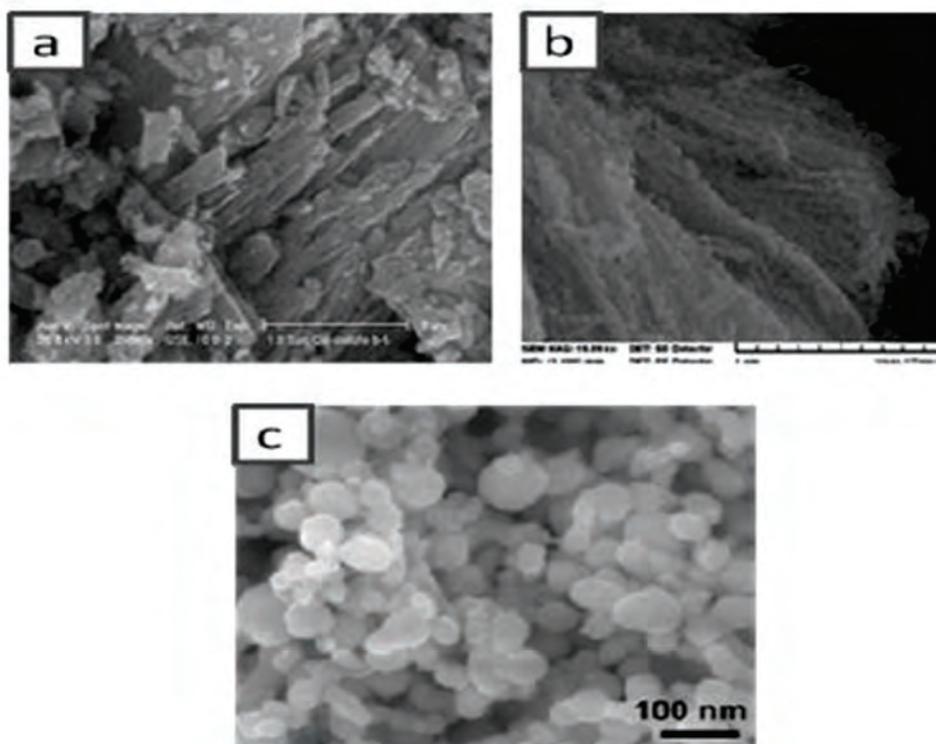


Fig 6.: SEM image of : (a) Cobalt oxalate (b) Cobalt powder at low magnification (c) Cobalt powder at higher magnification

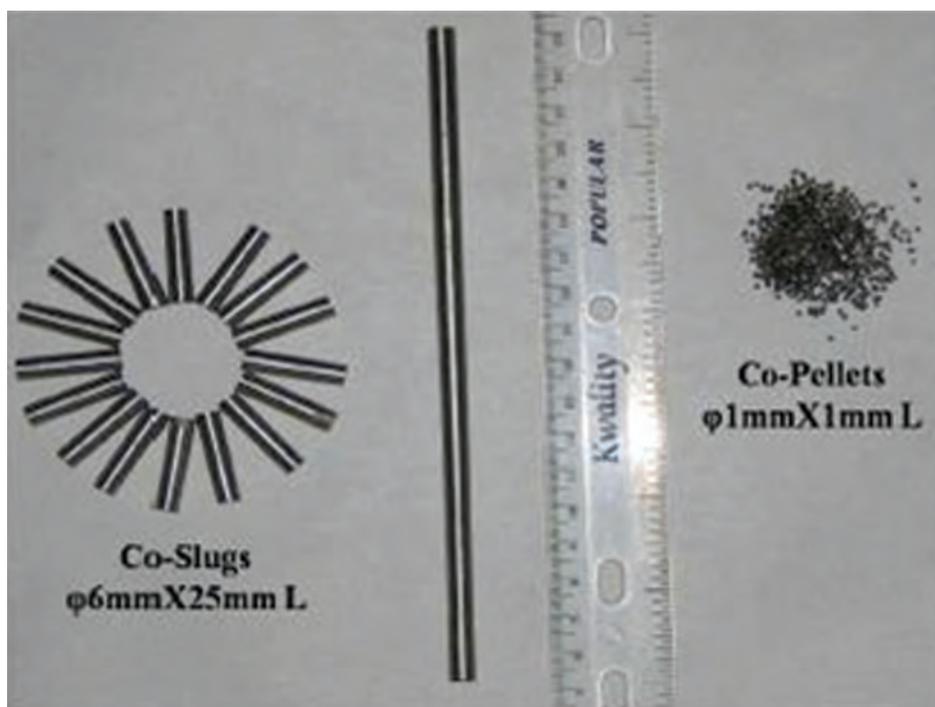


Fig 7. Ni plated cobalt shapes

a barrel having 3 mm holes and another for cobalt pellets with a barrel having 0.8 mm holes have been commissioned and used for nickel coating of the cobalt slugs and pellets by the nickel electro-plating technique. The coating thickness is around $10\ \mu\text{m}$. The final products are displayed in Fig. 7.

Conclusion:

The process described here has enabled the extraction of a valuable metal from what is essentially a waste material and its subsequent conversion into shapes of both economic and strategic significance to the nation. It has permitted import substitution of a commodity whose procurement otherwise faced uncertainties due to export embargos. The entire technology was developed in-house and the entire plant and machinery is also indigenous.

Acknowledgement

The project could not have succeeded without the invaluable contributions of Shri V.H. Bafna, Dr. M.V. Rane, Shri S.N. Bhandary, Shri S.P. Mhatre, Shri S.K. Gawai, Shri S.N. Kamble, Shri J. Varshney, Shri J.

Haider and Smt. R.J. Hadkar. The contribution of Shri S.B. Jawale and Shri J.J. Roy of CDM in design and manufacture of the multi-cavity die is gratefully acknowledged.

References

1. Sadanandam, R, Fonseca, M.F., Srikant, K., Sharma, A.K., Tangri, S.K. and Suri, A.K., 2008, Production of high purity cobalt oxalate from spent ammonia cracker catalyst, Hydrometallurgy, 91, pp. 28–34.
2. Alex, Pamela, Mishra, Prabhat and Suri, A.K., 2000 Studies on processing of an Alnico scrap, Mineral processing and extractive metallurgy review, 22, pp 547 – 565.
3. Bhaskar Paul, A.C. Bidaye, R.C. Hubli and A.K. Suri; Optimization of sintering parameters of submicron cobalt metal powder using Taguchi method; Journal of Metallurgical Engineering 1 (2012), 23-29.
4. Bhaskar Paul, Dheeraj Jain, A.C. Bidaye, I.G. Sharma and C.G.S. Pillai, Sintering kinetics of sub-micron sized cobalt powder ; Thermochemica Acta, 488 (2009), 54-59.